

INCORPORATING CO₂ SEQUESTRATION AND COALBED METHANE RECOVERY INTO HYDROGEN PRODUCTION FROM COAL - ECONOMICS AND ENVIRONMENTAL ASPECTS

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KEYWORDS: Hydrogen production, coal gasification, CO₂ sequestration

ABSTRACT

A hydrogen production process using pressure swing adsorption (PSA) for purification results in a concentrated CO₂ gas stream. In a typical natural gas steam reforming process this stream is used to fuel the reformer. However, because coal gasification takes place at high temperatures the synthesis gas contains very little CH₄ and other hydrocarbons, therefore, reforming is not required. An analysis was performed to examine hydrogen production via gasification of low sulfur western coal with CO₂ sequestration of the PSA off gas. This stream is then used to displace methane from unmineable coalbeds and the methane is utilized within the gasification-to-hydrogen system. Several processing schemes were evaluated: a reference case, a CO₂ sequestration only case, a maximum hydrogen production case, and a hydrogen/power coproduction case. The purpose of the analysis was to examine the technoeconomic feasibility, CO₂ emissions, and energy balance of these systems. This paper discusses the cases examined and presents the results of this study.

INTRODUCTION

A collaborative effort to study the feasibility of producing hydrogen from low Btu western coal with an emphasis on CO₂ sequestration and coal bed methane recovery was undertaken by National Renewable Energy Laboratory (NREL) and the Federal Energy Technology Center (FETC). Four cases which are outlined in Table 1 were studied in this analysis.

Table 1: Cases Examined

Case	Title	Description
1	reference case	coal gasification, shift, & H ₂ purification
2	CO ₂ sequestration only	reference case with CO ₂ sequestration only added
3	maximum H ₂ production	H ₂ production via the syngas, CO ₂ sequestration, & additional H ₂ production via steam methane reforming of the coalbed methane
4	H ₂ /power coproduction	H ₂ production via the syngas, CO ₂ sequestration, & power production via the coalbed methane

SYSTEM DESCRIPTION

Because Wyodak coal is inexpensive to produce and is available in an abundant supply, it was selected as a suitable low-rank Western coal for this study. The coal is assumed to be mined from the Wyoming region, gasified to produce hydrogen, then the CO₂-rich off gas is injected into unmineable coal beds. Coal gasification is via the Destec gasifier which is a two-stage entrained, upflow gasifier that operates at an exit temperature of 1,038°C (1,900°F) and a pressure of 2,841 kPa (412 psia). The feed is a coal/water slurry and for hydrogen production, the gasifier is oxygen blown in order to minimize the amount of nitrogen in the syngas.

The synthesis gas leaving the gasifier contains entrained particles of char and ash. Particulate removal is performed through cyclone separators and ceramic candle type hot gas filters. The coal gas is primarily comprised of H₂, CO, CO₂, and H₂O and, since there is less than 0.1 mol% CH₄, reforming of the syngas is not necessary. However, in order to maximize hydrogen production, shift reactors are needed to convert the carbon monoxide to hydrogen. Because the syngas from the gasifier contains approximately 1,400 ppm of H₂S, the majority of the sulfur must be removed prior to shift conversion. Hot gas clean up (HGCU) followed by a ZnO bed is the most economical sulfur removal choice because it avoids cooling and reheating the syngas stream, in addition to avoiding condensing out the majority of the steam that is required for shift conversion. The transport desulfurizer technology from the Piñon Pine Project located near Reno, Nevada was used in the HGCU process step. This technology has an absorber/regenerator system where sulfur compounds

are absorbed on a zinc oxide based sorbent. When the sorbent is regenerated, SO_2 is captured and converted to sulfuric acid. Because the gasifier operates at a high temperature, a steam cycle was incorporated into the process design. Stepwise cooling of the synthesis gas produced steam that was used to generate electricity or to fulfill the plant steam requirements. Finally, hydrogen purification is done using a pressure swing adsorption unit.

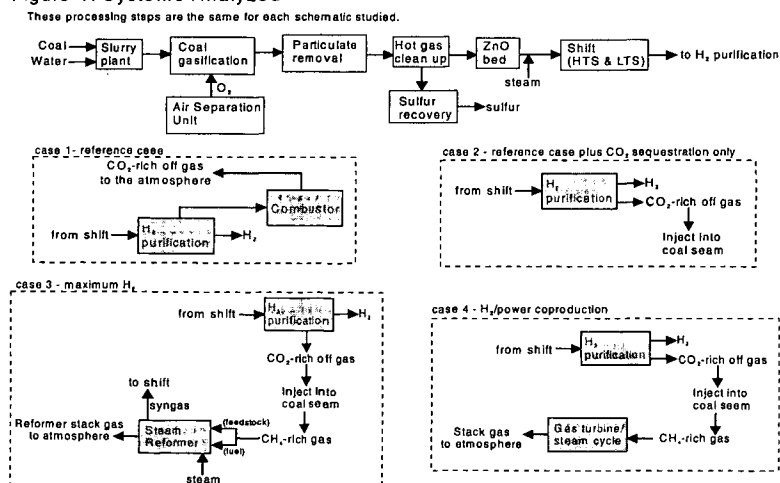
The analysis assumes that two molecules of CO_2 were injected for every one molecule of CH_4 released from the coalbed (Gunter *et al.*, 1996 and Hendriks, 1994). The off gas from the hydrogen purification unit containing primarily CO_2 (68 mol%; 93 wt%) was compressed from 2.6 MPa (372 psi) to a pressure of 8 MPa (1,160 psi). The analysis also assumed that new wells needed to be drilled and that they were connected by a CO_2 distribution system.

SCHEMES EXAMINED

In order to compare the economics as well as the overall CO_2 emissions from each schematic studied in this joint venture, a reference case was analyzed which included only the process steps associated with coal gasification, shift, and hydrogen purification (i.e., none of the steps associated with CO_2 sequestration or coalbed methane recovery were included in the reference case). Three other process schemes were examined in this study and compared to the reference case. Figure 1 depicts the reference case as well as the other three schemes (Note: The overall heat integration for each option is not shown.). The top portion of the figure shows the process steps that are the same for each schematic up to hydrogen purification while the operations inside the dashed boxes represent the steps that differ among the four options.

Scheme one represents the reference case (case 1). The PSA off gas is typically used to fuel the reformer in steam methane reforming plants but, due to the composition of the gasifier syngas, this scenario did not require a reformer. Therefore, the PSA off gas would be combusted, the heat would be used by another source (i.e., in producing steam), and the flue gas emitted to the atmosphere. The second scheme is the reference case with CO_2 sequestration only added to it and thus coalbed methane is not recovered (case 2). Scheme number three is maximum hydrogen production (case 3). The off gas is injected into the coal seam and a portion of the recovered methane is reformed to produce synthesis gas. This gas is then shifted and purified to produce more hydrogen. Part of the recovered coalbed methane is used to fuel the reformer. The fourth scheme is to produce hydrogen from the synthesis gas, to inject the CO_2 -rich off gas into the coalbed, and to produce power from the recovered methane (case 4). For this scenario, power is produced using a natural gas turbine and steam cycle.

Figure 1: Systems Analyzed



RESULTS - MATERIAL & ENERGY BALANCE

The material and energy balance for each case studied is given in Table 2. The coal feed rate is the same for each option and the resulting amount of hydrogen does not change except for the maximum hydrogen production case (case 3). Additionally, all of the cases examined, except maximum hydrogen production (case 3), produce some amount of power.

Table 2: Material & Energy Balances at 100% Capacity

Case	Coal (as received) (kg/hr)	Coalbed CH ₄ (kg/hr)	H ₂ (kg/hr)	Electricity required (MW)	Energy ratio
Reference	113,393	0	8,011	-12	0.83 ¹ 0.58 ²
CO ₂ sequestration only	113,393	0	8,011	-4	0.57
Maximum H ₂	113,393	47,366	18,739	3	0.67
H ₂ /power coproduction	113,393	36,419	8,011	-241	0.50

Energy ratio defined as (energy out of the system/energy into the system):

$$\frac{(H_2)(HHV_{H_2}) + (STM_{st})(\Delta H_{sh}) + e_{exp} + (off)(HHV_{off})}{(Coal_t)(HHV_{coal}) + (CH_4)(HHV_{CH_4}) + e_{imp}}$$

H₂ = hydrogen produced (kg)

HHV_{H₂} = higher heating value of hydrogen (GJ/kg)

STM_{st} = steam produced which is sold (kg)

ΔH_{sh} = enthalpy difference between incoming water and steam produced which is sold (GJ)

e_{exp} = exported electricity (GJ equivalents)

off = off gas produced (kg) - reference case only

HHV_{off} = higher heating value of off gas (GJ/kg) - reference case only

Coal_t = coal feed rate (kg)

HHV_{coal} = higher heating value of the coal (GJ/kg)

CH₄ = methane feed rate (kg)

HHV_{CH₄} = higher heating value of the methane (GJ/kg)

e_{imp} = imported electricity (GJ equivalents)

¹This is the energy ratio with an off gas energy credit.

²This would be the energy ratio if there were no off gas energy credit.

RESULTS - CO₂ BALANCE

To adequately determine the overall effect of CO₂ for each option studied, the CO₂ balance must incorporate CO₂ emissions in addition to those emitted from the process itself. For example, each case produces electricity, except for the maximum hydrogen production case (case 3), and for these cases (cases 1, 2, and 4) a CO₂ emissions credit must be taken for displacing electricity from the grid. Because the maximum hydrogen production case (case 3) requires some grid electricity, the system must be debited (rather than credited) with CO₂ emissions equivalent to the plant's net electricity requirement. Additionally, for the two options that recover coalbed methane (case 3 and 4), each of those systems must be credited with CO₂ emissions that are avoided from natural gas production and distribution via today's normal routes of gas and oil wells. Table 3 summarizes the CO₂ emissions for each of the cases examined.

Table 3: CO₂ Balance at 100% Capacity

Case	Overall CO ₂ to atm (kg/hr)	Avoided electricity CO ₂ (kg/hr)	Avoided natural gas CO ₂ (kg/hr)	Electricity CO ₂ (kg/hr)	Process CO ₂ (kg/hr)
Reference	195,707	-10,037	N/A	N/A	205,744
CO ₂ sequestration only	-3,667	-3,667	N/A	N/A	0
Maximum H ₂	65,985	N/A	-12,694	2,619	43,070
H ₂ /power coproduction	-109,065	-200,575	-9,760	N/A	101,270

Process CO₂ defined as:

Reference = flue gas resulting from combusting CO₂-rich PSA off gas

CO₂ sequestration only = none

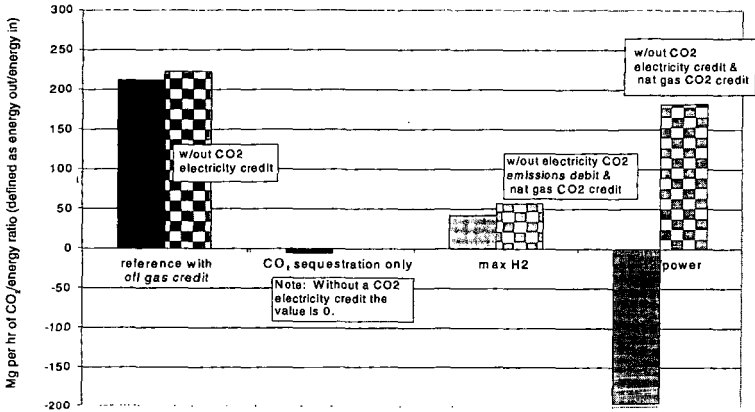
Maximum H₂ = CO₂ in the reformer flue gas

H₂/power coproduction = CO₂ in the natural gas combined cycle stack gas

For the reference case (case 1), the CO₂ emissions are primarily a result of the hydrogen production process. The overall CO₂ emissions for the CO₂ sequestration only case (case 2) are actually slightly negative instead of zero because of the CO₂ credit for the displaced grid electricity. The hydrogen/power coproduction case (case 4) also results in a negative amount of CO₂ emissions. This is due to the large credit in CO₂ emissions from displacing a significant quantity of grid electricity. In this analysis, grid electricity was assumed to be the generation mix of the mid-continental United States, which according to the National Electric Reliability Council, is composed of 64.7% coal and

coal-fired power plants generate large quantities of CO₂. There are still a large amount of process emissions from this system but these are overshadowed by the avoided CO₂ emissions. Even though the maximum hydrogen case (case 3) sequesters CO₂, some CO₂ is generated when the off gas is burned in the reformer. Also, some electricity is required for this case which results in additional CO₂ emissions. However, overall it is not correct to compare the emissions on a per system or a per amount of hydrogen produced basis because many of these cases generate power (refer to Table 2) and all of the cases produced energy in the form of steam. Additionally, for two of the cases (case 3 and 4), the additional hydrogen or power is produced from coalbed methane and the energy content of this feedstock must be taken into consideration. To correctly compare each system, they must be examined on an energy wide basis. If the CO₂ emissions were examined per the amount of hydrogen produced from each system then the results would be misleading. Therefore, the CO₂ emissions were divided by the energy ratio of the system and the results can be seen in Figure 2. For comparison, the CO₂ emissions were also plotted assuming that no CO₂ credits or debits were taken for grid electricity and natural gas production and distribution. It is evident that the only case that is greatly affected by this, and would most definitely be misrepresented, is the hydrogen/power coproduction case (case 4). Hydrogen/power coproduction (case 4) and CO₂ sequestration only (case 2) are the only cases that result in a negative amount of CO₂ emissions. However, the maximum hydrogen production case (case 3) does emit significantly less CO₂ than the reference case (case 1).

Figure 2: CO₂ Emissions per Energy Ratio @ 90% Capacity Factor



RESULTS - COST OF HYDROGEN

The plant gate hydrogen selling price was determined using a cash flow analysis with an after-tax internal rate of return (IRR) of 15%. However, because the hydrogen production plant must be located at the coal mining site in order to sequester CO₂ into unmineable coalbeds, it is not likely that the consumer will be “over the fence”. Therefore, the cost to store and transport the hydrogen must be added to the plant gate cost in order to determine the delivered cost of the hydrogen. For this study, because the hydrogen plant is assumed to be sited far from any users, two likely storage and transportation options were examined: (1) bulk delivery for a distance of 1,610 km (one way) and (2) pipeline delivery with 3 km to nearest infrastructure; no storage; an additional 1,610 km pipeline distance for delivery to end user for which the cost is shared by 5 companies. Table 4 gives the plant gate cost as well as the delivered cost for each of the cases examined in this study. The cheapest storage method for the bulk delivery option was determined to be liquid/rail based on previous work at NREL (Amos, 1998). The maximum hydrogen production and hydrogen/power coproduction cases (case 3 and 4) were found to be more economical than the reference case (case 1). Pipeline delivery added \$4.67/GJ to the plant gate cost and bulk delivery added \$8.78/GJ.

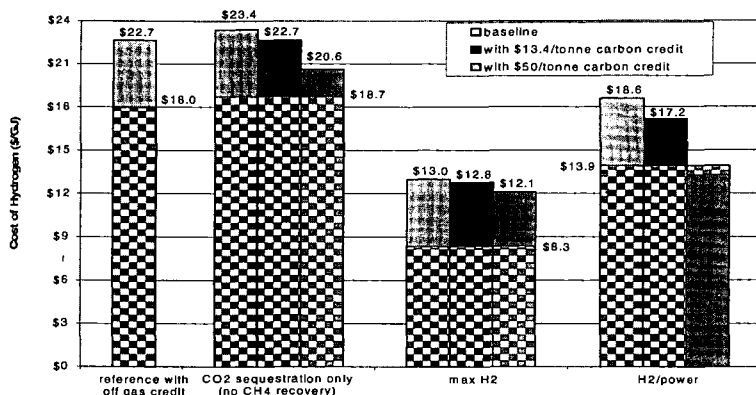
Table 4: Cost of Hydrogen

Case	Plant gate hydrogen selling price (\$/GJ)	Delivered cost of hydrogen (\$/GJ)	
		Bulk delivery (1,610 km - liquid/rail)	Pipeline delivery (1,610 km - shared)
Reference	17.98	26.76	22.65
CO ₂ sequestration only	18.72	27.50	23.39
Maximum hydrogen	8.34	17.12	13.01
H ₂ /power coproduction	13.92	22.70	18.59

RESULTS - CARBON TAX

By comparing the hydrogen selling price of the reference case (case 1) with that of the CO₂ sequestration only case (case 2), a carbon tax that would represent a break-even point was calculated. The hydrogen selling price for the CO₂ sequestration only case (case 2) would be reduced to \$17.98/GJ, the reference (case 1) with off gas credit case cost, if a carbon tax of \$13.4/tonne of carbon was mandated. Additionally, to examine the affect of a higher tax, a carbon tax of \$50/tonne of carbon was applied to the analysis. Figure 3 shows the plant gate selling price (denoted by the checkered sections), the cost of hydrogen for the baseline pipeline delivery option, and how the two carbon tax values affect the delivered cost of hydrogen for each of the four cases examined in this study. A carbon tax has the greatest effect on the hydrogen/power coproduction case (case 4). A \$50/tonne of carbon tax brings the delivered price of hydrogen below the plant gate selling price with the delivered cost being reduced from \$18.6/GJ to \$13.3/GJ. The delivered cost of hydrogen from the CO₂ sequestration only case (case 2) is reduced by \$2.8/GJ while a carbon tax has a small effect of the maximum hydrogen case (case 3) with a reduction of about \$1/GJ.

Figure 3: Delivered Cost of Hydrogen (Pipeline -1,610 km) with a Carbon Tax



CONCLUSIONS

Four process schemes were evaluated in this coal gasification, hydrogen production study. The economics favor sequestering CO₂, recovering coalbed methane, and making hydrogen or power (case 3 and 4). However, due to the CO₂ emissions generated from the steam methane reformer, additional hydrogen production via natural gas is not necessarily the most environmentally friendly option from a CO₂ standpoint (case 3). Coal fired power plants emit large quantities of CO₂, therefore optimizing hydrogen production with electricity generation, as in case 4, is a means of lowering the CO₂ emissions from power generation in the U.S. Because of the high temperatures, coal gasification to hydrogen production does not require a steam methane reforming step, and adding CO₂ sequestration only (case 2), results in almost no CO₂ being emitted to the atmosphere for a minimal cost. Mandating a carbon tax would make sequestering the CO₂ economically viable. However, for all of the cases examined in the analysis it should be noted that there is much debate about the fate of the sequestered CO₂ and its long term environmental effects.

ACKNOWLEDGEMENTS

We would like to acknowledge the Department of Energy's Office of Fossil Energy and Office of Energy Efficiency and Renewable Energy for funding this work. We would also like to recognize Harold Chambers, Diane Revay Madden, and Denny Smith at FETC and Walter Shelton at EG&G Technical Services of West Virginia who provided coal gasification data for this study.

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GEOTHERMAL POWER PRODUCTION UTILIZING SUPERCRITICAL CO₂ COMBINED WITH DEEP EARTH CARBON SEQUESTRATION

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KEYWORDS: hot-dry-rock (HDR) geothermal energy, heat mining using supercritical carbon dioxide, deep-earth carbon sequestration

ABSTRACT

For equivalent levels of electric power production, a deep man-made geothermal reservoir designed to supply the heat requirements for power generation would sequester, per unit time, about as much CO₂ as that produced by a typical coal-fired power plant. The deep earth carbon sequestration would be accomplished by the gradual diffusion of CO₂ into the unfractured rock mass surrounding the highly pressurized geothermal reservoir.

INTRODUCTION

A new engineered geothermal energy concept using supercritical CO₂ (SCCO₂) to both create the *man-made* geothermal reservoir and for heat transport to the surface is here proposed. This concept builds on the extensive Hot Dry Rock (HDR) research and development effort conducted by Los Alamos National Laboratory (LANL) at Fenton Hill, NM. This previous field testing convincingly demonstrated the viability of the HDR heat-mining concept, based on the results obtained from the production testing of two separate confined reservoirs for almost a year each. However, using SCCO₂ instead of water in a closed-loop HDR system offers three significant advantages over the original Los Alamos concept:

- The very significant wellbore density difference between the cold SCCO₂ in the injection well (about 0.96 g/cc) and the hot SCCO₂ in the production wells (about 0.39 g/cc) would provide a very large buoyant drive (i.e., thermal siphoning), markedly reducing the circulating pumping power requirements over those of a comparable water-based HDR system.
- The inability of SCCO₂ to dissolve and transport mineral species from the geothermal reservoir to the surface would eliminate scaling in the surface piping, heat exchangers, and other surface equipment.
- HDR reservoirs at temperatures in excess of 374°C (the critical temperature for water) could be developed without the problems associated with silica dissolution in water-based systems, potentially providing increased thermodynamic efficiency for the surface power-conversion equipment.

Thermodynamic and systems analyses show that SCCO₂, because of its unique properties, is nearly as good as water when used for heat mining from a confined HDR reservoir (see Brown, 2000). Even though the mass heat capacity of SCCO₂ is only two-fifths that of water, for equivalent reservoir operating conditions, the ratio of fluid density to viscosity (a measure of the reservoir flow potential) is 1.5 times greater for SCCO₂ than for water, primarily due to the viscosity of SCCO₂ which is 40% that of water. Therefore, the rate of geothermal energy production using SCCO₂ would be about 60% that of water. However, on a net power production basis, when pumping power requirements are considered, the power production from an SCCO₂-HDR system would almost equal that of a water-based HDR system.

The commercial development of this new renewable energy concept, given the ubiquitous worldwide distribution of the HDR geothermal resource, could be a significant contributor to providing clean, renewable sources of energy for the 21st century. Further, this new geothermal energy concept would help in mitigating global warming since a supercritical-CO₂-based HDR system would also sequester significant amounts of CO₂ deep in the earth by fluid diffusion into the rock mass surrounding the reservoir. To put this statement in perspective: Such an HDR power plant, based on long-term reservoir pressurization/fluid-loss studies carried out by LANL at Fenton Hill, would have the capability of continuously sequestering, by fluid diffusion into the rock mass surrounding the HDR reservoir, about as much CO₂ as that produced by a typical coal-fired power plant, each on a per MW-electric generation basis [24 tons of CO₂ per day per MW(e)].

THE HOT DRY ROCK CONCEPT AND RESOURCE BASE

HDR geothermal energy, which utilizes the natural heat contained in the earth's crust, can provide a widely available source of nonpolluting energy. The earth's heat represents an almost unlimited source of indigenous energy that could begin to be exploited worldwide within the next decade through the LANL-developed heat-mining concept. The feasibility of this concept has already been demonstrated by LANL through a sequence of field experiments at the Fenton Hill HDR test site extending over more than 20 years.

As depicted in Figure 1, hydraulic fracturing techniques developed by the oil industry would be used to create a very large stimulated volume of hot crystalline rock containing significant artificial permeability. This permeability would be created by pressure dilating the multiply interconnected array of pre-existing -- but hydrothermally resealed -- natural joints and fractures contained in a previously almost completely impermeable rock mass. This hydraulically stimulated region (the HDR reservoir) would then be connected to the surface through a pair of production wells, forming a closed-loop circulating system to transport the geothermal heat to the surface to be used in heating a secondary working fluid in a Rankine power cycle, or alternatively, to be used nearby for direct heating applications. In effect, we would be mining heat in a fashion analogous to the way other earth resources are obtained, but without any attendant pollution since the only thing that would be produced in this closed-loop process would be heat.

Numerous estimates place the accessible HDR resource base somewhere between 10 and 13 million quads in the US, and over 100 million quads worldwide (Tester et al., 1989). Figure 2 provides estimates of the geothermal temperature gradient distribution across the US and clearly shows that the moderate-grade (30° to 45°C/km) HDR resource is well distributed. Kron and Heiken (1980) estimate the high-grade US HDR resource base, with gradients greater than 45°C/km, to be in excess of 650,000 quads. Thus, on almost any basis, the amount of potentially usable thermal energy in the HDR resource is vast -- literally orders of magnitude larger than the sum total of all fossil and fissionable resources (see Figure 3 for a resource comparison on a worldwide basis). Even if only a small fraction of the accessible HDR resource base is ultimately extracted, the impact on the US energy supply could be far-reaching.

PRIOR RESEARCH

During the period from 1974 through 1995, LANL was actively engaged in field-testing and demonstrating the Hot Dry Rock (HDR) geothermal energy concept at their Fenton Hill HDR test site in the Jemez Mountains of north-central New Mexico (Brown, 1995a). This testing ended with the very successful demonstration of sustained energy production from the deeper HDR reservoir during a series of flow tests referred to as the Long-Term Flow Test (LTFT), conducted from April 1992 through July 1995 (Brown, 1994 and 1995b). Although that program has now ended, a vast amount of information was obtained concerning the characteristics and performance of confined HDR reservoirs during this extended period of testing. For instance, a recent report (Brown, 1999) summarizes the data from the LTFT supporting the existence and long-term stability of a highly pressurized region of jointed rock at a depth of 3.6 km, which is quite germane to studying the deep sequestration of carbon dioxide in basement rock associated with an HDR geothermal power-production system.

THE SCCO₂-HDR CONCEPT

In this new concept for engineered geothermal reservoirs, which embodies much of the original HDR concept developed and demonstrated by LANL, SCCO₂ would be used for both the fracturing fluid and the heat transport fluid for deep-earth heat-mining systems. As envisioned, a three-well HDR system -- two production wells and one injection well -- would be employed to best access the fractured reservoir region (Brown and DuTeaux, 1997). As shown schematically in Figure 1, the heat contained in the hot geofluid would be transferred to a secondary working fluid in a high-pressure heat exchanger included as part of the surface power plant.

A major contributing factor to the enhanced performance of an SCCO₂-HDR system is the very significant buoyant drive across the reservoir, arising from the marked density contrast between the hot fluid rising in the production wells and the cold, much more dense fluid in the injection well. For example, for an appropriate set of SCCO₂ surface operating conditions for the HDR reservoir depicted in Figure 1 -- a mean injection pressure of 30 MPa at 40°C and a surface production backpressure of 30 MPa at 250°C, the mean fluid density in the injection wellbore would be 0.96 g/cc and the corresponding mean fluid density in the production wellbores would be 0.39 g/cc, providing a density difference of about 0.57 g/cc. At a reservoir depth of 4 km, this augmented buoyant drive provided by using SCCO₂ instead of water as the geofluid would add an additional 22 MPa (3200 psi) to the pressure differential driving fluid across the reservoir. For the case of laminar flow which is the accepted flow regime in HDR reservoirs, this would more than double the production flow rate compared to a water-based HDR system with the same reservoir flow impedance and injection pressure, potentially providing a thermal power potential exceeding that of an equivalent water-based HDR system.

RESERVOIR CREATION

The engineered HDR reservoir region, probably approaching an ultimate volume of 1/2 cubic kilometer or more, would be created by hydraulically fracturing a deep region of essentially impermeable, hot, crystalline rock using SCCO_2 instead of water as the fracturing fluid. This would be accomplished by pumping SCCO_2 from the surface down a high-pressure tubing string, and injecting this fluid into a packed-off (i.e., pressure-isolated) interval of openhole wellbore for a period of several weeks or more, at a rate in the range of 20 to 40 kg/s.

Initially, as the pressure in the packed-off interval rapidly increases, one or more of the more favorably oriented natural joints intersecting the wellbore would start to open under a combination of tensile (hoop) stresses at the wellbore surface and normal opening stresses from fluid invasion into the somewhat more permeable (than the adjacent rock) hydrothermally sealed natural joints. As pumping continues, these joints would progressively open and interconnect, forming a multiply connected region of pressure-dilated joints in the rock mass surrounding the packed-off wellbore interval, thus creating the fractured HDR reservoir.

Based on over 20 years of reservoir testing at Fenton Hill, NM, this opening of an array of natural joints is in stark contrast with the originally envisioned formation of one or more large, near-vertical, penny-shaped fractures created by hydraulic fracturing (Brown, 1995a). Based on the Laboratory's extensive experience with hydraulic fracturing of deep basement rock using water, there appears to be no limitation to using SCCO_2 for similar operations. It should be noted that hydraulic fracturing of sedimentary formations using SCCO_2 , as reported by Yost et al. (1994), is now routinely done to increase the productivity of petroleum reservoirs where special reservoir conditions warrant this type of stimulation to minimize formation damage from water-based fracturing fluids.

POST-HYDRAULIC-FRACTURING FLUID COMPOSITION IN THE RESERVOIR REGION

From laboratory measurements on core samples of Precambrian crystalline rock obtained from depths between 1.2 and 2.8 km at Fenton Hill, a mean in-situ rock mass porosity of 0.9×10^{-4} has been determined (Simmons and Cooper, 1977). In contrast, following reservoir creation by hydraulic fracturing and the accompanying dilation of the pressure-stimulated array of joints, the mean reservoir porosity was about 1.2×10^{-3} [24,700 m^3 of water injected into a pressure-accessible volume of 20 million m^3 (Brown et al., 1999)]. Therefore, using an analogy to the deeper Fenton Hill HDR reservoir, the fracture volume occupied by the SCCO_2 would be about 13 times greater than the initial microcrack pore volume in the rock mass. For this situation, the SCCO_2 would tend to dissolve almost all of the original pore fluid (essentially a brine), with the mineral constituents previously dissolved in the pore fluid being left behind as mineral precipitates. Figure 4 shows the solubility, at 250°C, of water in SCCO_2 and SCCO_2 in water as a function of pressure. For an HDR reservoir with a rock temperature of 260°C at a depth of 4 km, and with a surface injection pressure of 30 MPa, one would anticipate about a 24 mol% solubility of water in SCCO_2 . This solubility is equivalent to a 10% solubility by weight, which would imply that all the previously existing pore fluid within the microcrack pore structure of the rock would end up being dissolved by the SCCO_2 diffusing into the rock mass.

CO₂ SEQUESTRATION IN THE ROCK MASS SURROUNDING THE HDR RESERVOIR

Again, from experience gained from extensive field testing of the deeper HDR reservoir at Fenton Hill, the fluid loss from a 1/2 cubic kilometer pressure-stimulated reservoir volume, at a mean reservoir injection pressure of 30 MPa (4350 psi) above hydrostatic, is predicted to be about 3 kg/s for a 10-MW(e) power system, which is equivalent to 100,000 tons per year. Although not a very large number in absolute terms, over the predicted 20-year lifetime of a suitably engineered HDR reservoir, this diffusional loss of SCCO_2 into the rock mass immediately adjacent to the HDR reservoir would be very significant -- about 2 million tons of CO_2 sequestered deep in the earth for each 10-MW(e) HDR power plant. This is in addition to the 48,000 ton inventory of SCCO_2 circulating through the reservoir and the surface power plant for such a 10-MW(e) HDR power system.

This leads to an ancillary benefit at the periphery of the HDR fractured region, where the SCCO_2 would be slowly diffusing outward to the far field from the pressurized reservoir. In the surrounding rock mass, the pre-existing water-filled network of interconnected microcracks would be slowly flushed with SCCO_2 , leaving behind mineral precipitates which would tend to slowly plug off the microcrack porosity and seal the reservoir boundaries over time -- which, from the normal point of view, are almost impermeable already (with a permeability in the range of several hundredths of a microdarcy).

SUMMARY AND CONCLUSIONS

In a confined reservoir, which is one of the unique characteristics of a true man-made HDR reservoir, as contrasted with a natural hydrothermal geothermal reservoir, the chemistry and/or

nature of the circulating fluid can be specified by the operator (Brown et al., 1999). For this reason, the choice of SCCO₂ as the working fluid is possible, and alters considerably the potential for designing unique features into such engineered geothermal systems.

As an ancillary benefit from the standpoint of carbon sequestration, the slow diffusional loss of SCCO₂ from the pressurized HDR reservoir region outward into the surrounding unfractured -- and therefore *confining* -- rock would, over the long term, provide a considerable amount of carbon storage within the microcrack volume of this rock mass.

In this preliminary study of the SCCO₂-HDR concept, it was not possible to consider all the ramifications or nuances of using a geofluid other than water as the heat transport fluid in an engineered heat-mining concept. However, the advantages of using SCCO₂ in a power-producing man-made HDR geothermal system appear to be considerable.

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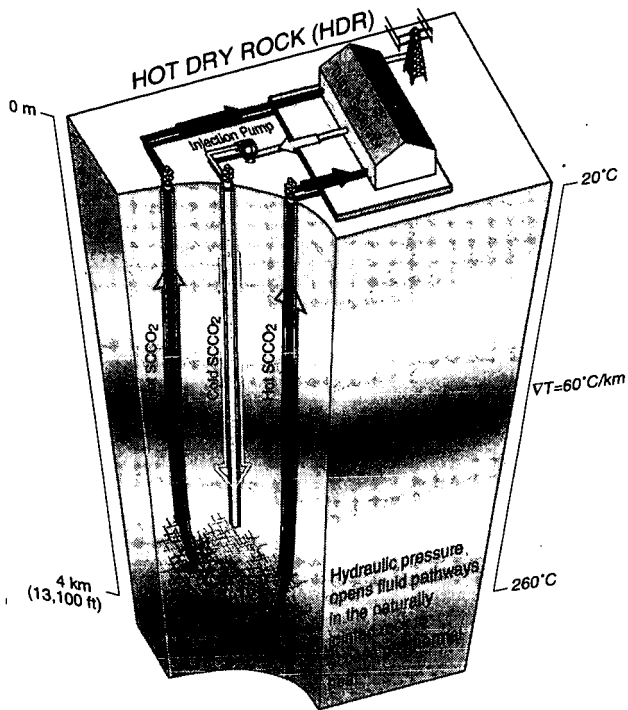


Figure 1: HDR-SCCO₂: A System Engineered for Geothermal Heat Mining Using Supercritical CO₂.

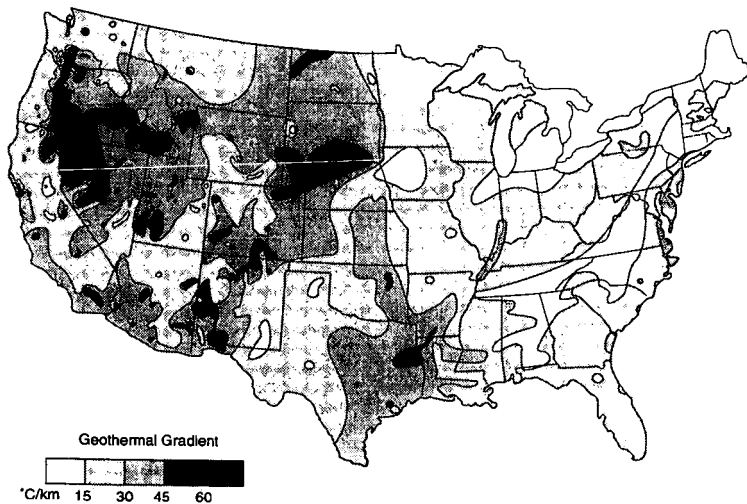


Figure 2: The Distribution of Geothermal Temperature Gradients in the "Lower 48" States.

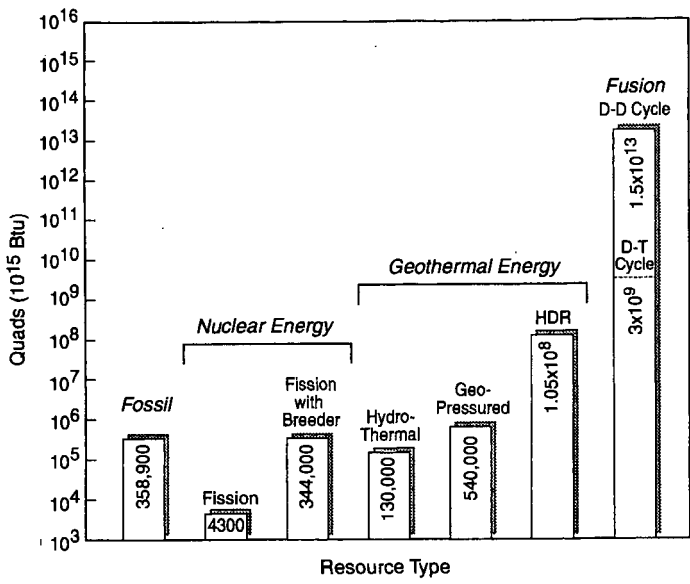


Figure 3: Worldwide nonrenewable resources.

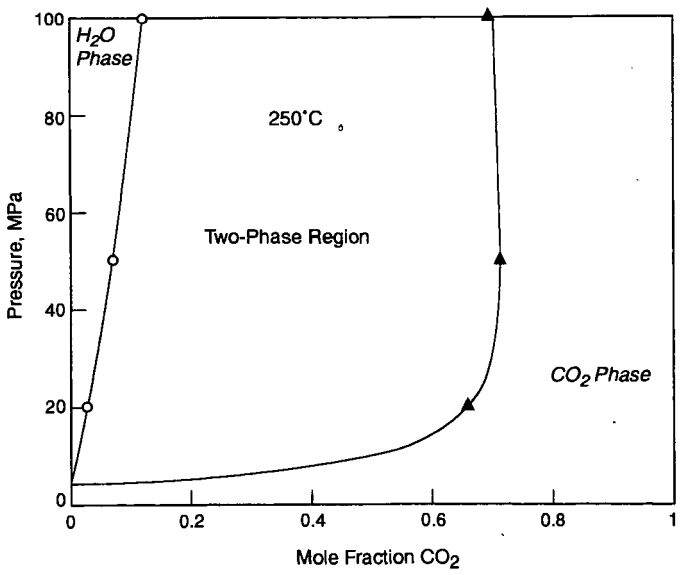


Figure 4: Phase diagram for CO₂ + H₂O at 250°C. Adapted from Shyu et al. (1997).

Tri-reforming: A New Process Concept for Effective Conversion and Utilization of CO₂ in Flue Gas from Electric Power Plants

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KEYWORDS: Tri-reforming, CO₂ Conversion, Flue Gas, Power Plants

INTRODUCTION

CO₂ conversion and utilization are a critically important element in chemical research on sustainable development. The prevailing thinking for CO₂ conversion and utilization begins with the use of pure CO₂, which can be obtained by separation. In general, CO₂ can be separated, recovered and purified from concentrated CO₂ sources by two or more steps based on either absorption or adsorption or membrane separation. These separation and purification steps can produce pure CO₂ from flue gases of power plants but add considerable cost to the CO₂ conversion or sequestration system [DOE/OS-FE, 1999]. Even the recovery of CO₂ from concentrated sources requires substantial energy input [Weimer et al., 1996]. According to US DOE, current CO₂ separation processes alone require significant amount of energy which reduces a power plant's net electricity output by as much as 20% [DOE/FE, 1999a]. While new technology developments could make this recovery easier to handle and more economical to operate in power plants, it is highly desirable to develop novel ways to use CO₂ in flue gases without separation.

SOURCES OF CO₂ EMISSIONS

A recent paper showed the data on CO₂ emissions from the consumption of fossil fuels during 1980-1997 in the world based on government reports on statistics [EIA/IEO, 1998, 1999]. The three major fossil fuels used worldwide are coal, petroleum, and natural gas. A very large amount of CO₂ is emitted every year, and the total amount of annual emissions is also increasing rapidly. The current top 10 major producers of CO₂ in terms of total annual emission include US, China, Russia, Japan, India, Germany, UK, Canada, South Korea, and Italy. CO₂ emissions from many other countries, particularly developing countries, are increasing rapidly.

Table 1 CO₂ Emissions from Different Sectors in the U.S. (in Million Metric Tons of Carbon)

CO ₂ Emissions Sources	1980	1985	1990	1995	1997
CO ₂ from Residential Sector	248.4	245.8	253.1	270.3	286.5
CO ₂ from Commercial Sector	178.3	189.7	206.8	217.9	237.2
CO ₂ from Industrial Sector	484.6	424.7	454.1	465	482.9
CO ₂ from Transportation Sector	378.1	384.4	432.1	458.5	473.1
CO ₂ from End-Use Total	1289.4	1244.6	1346.1	1411.7	1479.6
CO ₂ from Electric Utilities*	418.4	439	476.9	495.3	523.4

*Electric Utility emissions are distributed across end-use sectors.

Sources: DOE, EIA, 1998, 1999

Table 1 summarizes the CO₂ emissions from different sectors in the U.S. [EIA/AER, 1998, 1999]. A clear trend is that all the end-use sectors of energy are major contributors of CO₂, and electric power industry is no longer the only major CO₂ emitter. In other words, everyone in the society is responsible for the increased CO₂ production, either by using electricity in various places and by consuming fuels for transportation and for other purposes. Table 2 specifically indicates the CO₂ emissions from the U.S. electricity-generating units in electric utilities and non-utilities based on coal, natural gas and petroleum [EIA/AER, 1998, 1999]. Coal is the dominant fossil fuel for the electricity-generating units. On the other hand, it is projected that the share of natural gas-fired units will increase significantly in the near future, due to the heightened concerns for environmental issues and the fact that natural gas is viewed as a premium fuel and is environmentally cleaner than either coal or petroleum.

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Table 2. CO₂ Emission from Electricity-Generating Units in the U.S. (in Million Metric Tons of Carbon)

CO ₂ Emissions Sources	1990	1995	1997
Coal-Fired Units at Electric Utilities	409.9	434.3	471.3
Petroleum-Fired Units at Electric Utilities	25.3	13.0	15.0
Gas-Fired Units at Electric Utilities	39.2	44.5	36.0
Other Units at Electric Utilities	1.2	0.8	1.0
Emissions at Electric Utilities, Total	475.5	492.7	523.4
Coal-Fired Units at Nonutilities	17.8	24.6	25.3
Petroleum-Fired Units at Nonutilities	4.3	7.3	7.4
Gas-Fired Units at Nonutilities	39.2	57.6	53.2
Other Units at Nonutilities	37.4	45.9	48.4
Emissions at Nonutilities, Total	98.7	135.5	134.4
CO ₂ from Coal-Fired Units, Total	427.7	458.9	496.6
CO ₂ from Petroleum-Fired Units, Total	29.6	20.3	22.4
CO ₂ from Gas-Fired Units, Total	78.4	102.1	89.3
CO ₂ from Other Units, Total	38.5	46.8	49.4
Total CO ₂ Emissions from Generators	574.2	628.1	657.7

Sources: DOE, EIA, 1998, 1999

ADVANTAGES OF USING FLUE GAS FOR CO₂ CONVERSION

As can be seen from Table 2, flue gases from fossil fuel-based electricity-generating units represent the major concentrated CO₂ sources in the US. If CO₂ is to be separated, as much as 100 megawatts of a typical 500-megawatt coal-fired power plant would be necessary for today's CO₂ capture processes based on the alkanolamines [DOE/FE, 1999a]. Therefore, it would be highly desirable if the flue gas mixtures can be used for CO₂ conversion but without pre-separation of CO₂. Based on our research, there appears to be a unique advantage of directly using flue gases, rather than pre-separated and purified CO₂ from flue gases, for the proposed tri-reforming process.

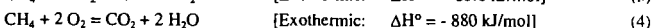
Typical flue gases from natural gas-fired power plants may contain 8-10% CO₂, 18-20% H₂O, 2-3% O₂, and 67-72% N₂; typical flue gases from coal-fired boilers may contain 12-14 vol% CO₂, 8-10 vol% H₂O, 3-5 vol % O₂ and 72-77% N₂ [Miller and Pisupati, 1999]. The typical furnace outlet temperature of flue gases is usually around 1200°C which will decrease gradually along the pathway of heat transfer, while the temperature of the flue gases going to stack is around 150°C [Miller and Pisupati, 1999]. Current toxic emission control technologies can remove the SO_x, NO_x and particulate matter effectively, but CO₂ and H₂O as well as O₂ remain largely unchanged.

In the proposed tri-reforming process, CO₂ in the flue gas does not need to be separated. In fact, H₂O and O₂ along with CO₂ in the waste flue gas from fossil-fuel-based power plants will be utilized for tri-reforming of natural gas for the production of synthesis gas.

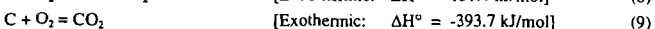
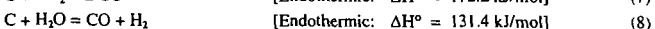
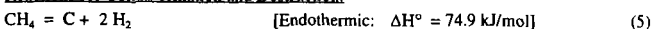
PROPOSED TRI-REFORMING PROCESS

The tri-reforming refers to simultaneous oxy-CO₂-steam reforming of natural gas (eqs. 1-4). It is a synergetic combination of endothermic CO₂ reforming (eq. 1) and steam reforming (eq. 2) and exothermic partial oxidation of methane (eqs. 3 and 4).

Tri-reforming of Natural Gas:



Reactions for Coke Formation and Destruction:



The tri-reforming (Figure 1) is an innovative approach to CO₂ conversion using flue gases for syngas production. Coupling CO₂ reforming and steam reforming can give syngas with desired H₂/CO ratios for methanol (MeOH) and Fischer-Tropsch (F-T) synthesis. Steam reforming is widely used in industry for making H₂ and syngas [Rostrup-Nielsen, 1993; Armor, 1999; Gunardson and Abrardo, 1999]. When CO-rich syngas for oxo synthesis and syngas with H₂/CO ratio of 2 are needed for F-T synthesis and methanol synthesis, steam reforming alone can not give the desired H₂/CO ratio [Gunardson, 1998]. Steam reforming gives too high a H₂/CO ratio (≥ 3) and thus need to import CO₂ for making syngas with H₂/CO ratios of 2 or lower.

CO₂ reforming (dry reforming) of CH₄ has attracted considerable attention worldwide [Ashcroft et al., 1991; Rostrup-Nielsen et al., 1993], and the research up to 1998 has been reviewed [Bradford and Vannice, 1998]. A simple estimate of energetics indicates that CO₂ reforming is 20% more endothermic than steam reforming (eq. 2 vs eq. 1), and so it does cost more energy. However, it can be done and is indeed necessary for adjusting H₂/CO ratio for making MeOH or F-T synthesis gas. There are two industrial processes that utilizes this reaction, including SPARG [O'Connor and Ross, 1998; Gunardson, 1998] and Calcor [Teuner, 1987; Kurz and Teuner, 1990]. CO₂ reforming of methane suffers from a major problem of carbon formation (eqs. 5 and 6), particularly at elevated pressures [Song et al., 2000; Sinivasa et al., 2000]. When CO₂ reforming is coupled to steam reforming, this problem can be effectively mitigated. This carbon formation in CO₂ reforming can be reduced by the addition of oxygen.

Direct partial oxidation of CH₄ to produce syngas [Dissanayake et al., 1991; Hickman et al., 1993] and partial combustion of CH₄ for energy-efficient autothermal syngas production [Pena et al., 1996] are being explored. These reactions are important but the catalytic partial oxidation is more difficult to control. The major operating problems in catalytic partial oxidation are the over-heating or hot spot due to exothermic nature of the oxidation reactions, and consequently coupling the exothermic reaction with an endothermic reaction could solve this problem [Ruckenstein and Hu, 1998].

The combination of dry reforming with steam reforming can accomplish two important missions: to produce syngas with desired H₂/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming. Integrating steam reforming and partial oxidation with CO₂ reforming could dramatically minimize or eliminate carbon formation on reforming catalyst thus increase catalyst life and process efficiency. Therefore, the proposed tri-reforming can solve two important problems that are encountered in individual processing. The incorporation of O₂ in the reaction generates heat in situ that can be used to increase energy efficiency and O₂ also reduces or eliminates the carbon formation on the reforming catalyst. The tri-reforming can thus be achieved with natural gas and flue gases using the 'waste heat' in the power plant and the heat generated in situ from oxidation with the O₂ that is already present in flue gas.

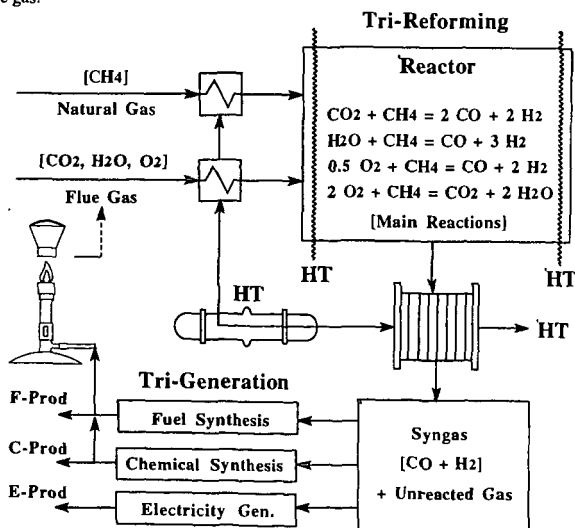


Figure 1. Conceptual design of proposed tri-reforming process in the recently proposed CO₂-based tri-generation system (Version 2 in May 2000).

As illustrated in Figure 1, the tri-reforming is the key step in the recently proposed CO₂-based tri-generation of fuels, chemicals, and electricity [Song, 1999, 2000]. In principle, once the syngas with desired H₂/CO ratio is produced from tri-reforming, the syngas can be used to produce liquid fuels by established routes such as Fischer-Tropsch synthesis, and to manufacture industrial chemicals by methanol and oxo synthesis. Syngas can also be used for generating electricity either by IGCC type generators or by using fuel cells.

The proposed tri-reforming concept is consistent, in general, with the goals of Vision 21 EnergyPlex concept [DOE/FETC, 1999b, 1999c] being developed by the U.S. DOE. The goals of Vision 21 EnergyPlex (plants) include greater efficiency of power generation (>60% with coal, >75% with natural gas), greater overall thermal efficiency (85-90%), near zero-emissions of traditional pollutants, reduction of greenhouse gas (40-50% reduction in CO₂ emission), and coproduction of fuels [DOE/FE, 1999b].

The challenges and feasibility issues and related literature information have been discussed recently [Song, 1999, 2000]. Current flue gases contain inert N₂ gas in high concentrations, and thus the conversion process design requires the considerations on how to dispose inert gas. It is possible that oxygen-enriched air or oxygen will be used in power plants in the future. If that becomes a reality, then the proposed tri-reforming process will be even more attractive because of much lower inert gas concentration and thus higher system efficiency. Another challenge is how to deal with the small amounts of NO_x, SO_x and other toxic substances that are present in most flue gases.

IS TRI-REFORMING FEASIBLE?

We have not found any previous publications or reports on reforming using flue gases or CO₂ conversion using flue gases related to the proposed concept [Song, 1999, 2000]. Our computational thermodynamic analysis shows there are benefits of incorporating steam (H₂O) and oxygen (O₂) simultaneous in CO₂ reforming of natural gas or CH₄ [Pan et al., 1999; Pan and Song, 2000]. On the other hand, some recent laboratory studies with pure gases have shown that the addition of oxygen to CO₂ reforming [Vernon et al., 1992; Choudhary et al., 1995; O'Connor and Ross, 1998; Ruckenstein and Hu, 1998] or the addition of oxygen to steam reforming of CH₄ [Choudhary et al., 1998] can have some beneficial effects in terms of improved energy efficiency or synergetic effects in processing and in mitigation of coking. A feasibility analysis by calculation showed that utilizing CO₂/H₂O/O₂/CH₄ for making synthesis gas is feasible [Tjajopoulos and Vasalos, 1998]. Inui and coworkers have studied energy-efficient H₂ production by using mixture of pure gases including CH₄, CO₂, H₂O and O₂ [Inui et al., 1995]. Choudhary and coworkers have reported on their laboratory experimental study on simultaneous steam and CO₂ reforming of methane over Ni/MgO-SA in the presence of O₂ at atmospheric pressure; they have shown that it is possible to convert methane into syngas with high conversion and high selectivity for both CO and H₂ [Choudhary et al., 1998]. Ross and coworkers have shown that a Pt/ZrO₂ catalyst is active for steam and CO₂ reforming combined with partial oxidation of methane [Hegarty et al., 1998]. Therefore, the proposed tri-reforming of flue gas from power plants appears to be feasible and safe, although its demonstration requires detailed experimental studies, computational analysis as well as engineering evaluations.

CONCLUDING REMARKS

A new process concept, tri-reforming, is proposed for effective conversion and utilization of CO₂ in the waste flue gases from fossil fuel-based power plants in the 21st century. The CO₂, H₂O and O₂ in the flue gas need not be pre-separated because they will be used as co-reactants for the tri-reforming of natural gas. In the tri-reforming (simultaneous oxy-CO₂-steam reforming) process, the flue gas and natural gas are used as chemical feedstock for production of synthesis gas (CO+H₂) with desired H₂/CO ratios.

The proposed tri-reforming is a synergetic combination of CO₂ reforming, steam reforming, and partial oxidation of natural gas. The tri-reforming process solves some of the major problems in CO₂ reforming, in steam reforming, and in partial oxidation. It also makes use of the 'waste heat' in the power plant and heat generated in situ from oxidation with the O₂ that is already present in flue gas. This tri-reforming process could be applied, in principle, for natural gas-based or coal-based power plants and IGCC power plants.

Another important feature of the proposed tri-reforming is that this is the first innovative approach to conversion and utilization of CO₂ in flue gases from power plants without CO₂ separation. Many

questions remain to be answered, and further research is needed in order to establish and demonstrate this new process concept.

Acknowledgments

The author wishes to thank his coworkers (Mr. W. Pan and Dr. S. T. Srinivas) at PSU and Dr. John Armor of Air Products and Chemicals Inc. for helpful discussions on reforming. The author is also grateful to his colleagues (B. Miller and S. Pisupati) for helpful discussions on power plant flue gas.

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**THE POTENTIAL ROLE
OF GEOLOGIC STORAGE AND CARBON DIOXIDE
IN A SUSTAINABLE FOSSIL FUELS FUTURE**

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Frank M. Ferrell, U.S. Department of Energy

James K. Carey, Energetics, Incorporated

ABSTRACT

Various geologic settings are beginning to be examined as possible sinks for storage of CO₂. These include depleting and depleted oil and gas reservoirs, deep unmineable coal seams, and deep saline or brine formations. It is well known that there are many methanogens in nature which convert CO₂ to CH₄. Some of these are extremeophiles, existing at high temperatures and pressures. At least one has been the subject of genome mapping. It is also known that "directed development" is a methodology that is being utilized to develop "designer microbes" with selected or enhanced traits. The concept described here is that through a coordinated biological, chemical, and geophysical effort, either designer microbes or biomimetic systems can be developed to produce closed-loop fossil fuel systems. In such systems, geologic repositories of CO₂ could be converted to CH₄, thereby closing the fuel cycle in a sustainable manner.

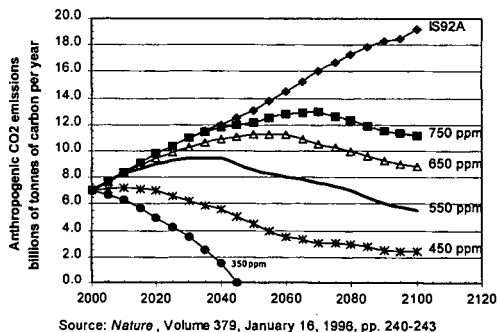
Keywords: carbon sequestration, global climate change, methanogenesis

INTRODUCTION

This paper is an early output from an ongoing investigation of the state-of-the-art related to the concept of geologic storage of CO₂ with subsequent conversion to methane. In most of the areas reviewed, the research has been performed for reasons other than that which is the focus of this paper—carbon management in response to global climate change. For example, hydrocarbon seeps have been studied to develop better oil exploration techniques, thermal vents have been studied to better understand their environmental impacts, and hydrocarbon emissions from natural sources have been studied for knowledge about global climate change.

We believe that there is a need and opportunity to bring together researchers and knowledge from diverse fields to identify and conduct focused scientific and technologic research to determine the potential of options discussed in this paper along with other novel concepts that may emerge.

Due to growing concern about the effects of increasing carbon dioxide in the atmosphere, the United States and 160 other countries ratified the Rio Mandate, which calls for "... stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system." While the level of greenhouse gases that represents "stabilization" is open to debate, a range of 350-750 parts per million (ppm) is widely discussed. As shown in the various scenarios in Figure 1, all of these scenarios are significantly lower than a "business as usual" scenario (IS92A). When one considers the anticipated growth in the global population and the global economy over the next 50-100 years, even modest stabilization will require enormous amounts of fossil energy with very low greenhouse gas emissions. Many energy producers are now recognizing the major role that carbon sequestration must play if we are to continue to enjoy the economic and energy security benefits which fossil fuels bring to the world's energy mix.



**Figure 1. Scenarios for the Stabilization of
Global Carbon**

Under virtually any stabilization and market scenario, fossil fuels will remain the mainstay of energy production for the foreseeable future. To achieve any level of atmospheric stabilization that is ultimately deemed acceptable, there are three basic approaches: 1) reduce the carbon content of fuels, 2) improve the efficiency of energy use, and 3) capture and sequester the carbon. The approach of sequestration is comparatively new, and is now discussed as both a technology and policy option to mitigate global climate change (1). In the United States, sequestration has joined the first two approaches within the Department of Energy (DOE) as a valuable option, with funding of sequestration R&D activities (2). A report prepared jointly by the U.S. DOE Office of Science and the DOE Office of Fossil Energy (DOE/FE) identified five pathways to sequestration (3).

- Capture and sequestration
- Sequestration in geologic formations
- Ocean sequestration
- Sequestration in terrestrial ecosystems (soils and vegetation)
- Chemical, biological and other advanced concepts for CO₂ fixation or reuse.

Within the DOE/FE, the Carbon Sequestration Program has further delineated these research pathways and the current R&D activity within the pathways (4). Figure 2 shows the program's research areas. Together they cover the carbon sequestration life cycle of capture, separation, transport, and storage or reuse. A recent report by DOE/FE outlines the national needs, benefits, strategy, plans, and milestones for the program (5). Within this context is an emphasis on enhancing natural CO₂ sequestration processes, including enhancement of storage in various geologic formations, in soils and biomass, and through enhanced mineralization.

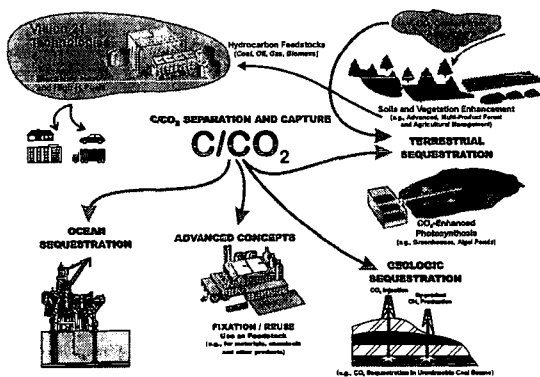


Figure 2. Carbon Sequestration Pathways

DISCUSSION

Natural CO₂ reservoirs are relatively common. They are in fact commercially exploited for CO₂ production for commodity use. In addition to these comparatively pure CO₂ reservoirs, CO₂ is found in many other formations. Reservoirs of various kinds exist throughout the world containing mixtures of CO₂, methane, and various other fluids. Many of these geologic settings are being examined as possible sinks for storage of CO₂. These include depleting and depleted oil and gas reservoirs, deep unmineable coal seams, and deep saline or brine formations. In one current commercial project CO₂ is being sequestered under the North Sea (1). The Norwegian oil company Statoil is recovering CO₂ from natural gas processing, and injecting approximately one million tons per year of CO₂ into a sandstone layer. This is a saline formation under the sea associated with the Sleipner West Heirndel gas reservoir. The amount being sequestered is equivalent to the output of a 250-MW gas-fired power plant.

Methanogenesis is a biological process which is widely found in nature. Methanogenic bacteria generate methane by several pathways, principally the fermentation of acetate and the reduction of CO₂ (6)(7). Generally a consortium, or food chain of microbial organisms, operates together to effect a series of biochemical reactions in the production of methane in energy-yielding cellular processes. Methanogens are anaerobic bacteria of the family Archaea, and are found in such diverse environments as landfills, digestive systems of animals, in deep ocean vents, and in coal seams. Chemosynthetic communities are found in close association with cold hydrocarbon seeps, for example, and demonstrate complex relationships that include the mineralization of CO₂ as well as methanogenesis (8). In one location, sampling of hydrocarbon gases from ocean-floor cold hydrocarbon seeps in Monterey Bay, California suggest that most of the methane produced is microbial in origin (9). In coal seams, methanogens may increase coalbed methane production. Laboratory study of microbially enhanced coalbed methane processes indicate that microbial consortia can increase gas production through conversion of coal and enhancement of formation permeability, leading to the potential for substantially increased methane production (10).

In general, methane in the earth's crust may be formed by both biogenic (that is, the conversion of organic matter) and abiogenic processes. The vast majority appears to be biogenic in origin, and results from a combination of microbial production and thermogenic processes (11). It is believed that 20% of the natural gas in the earth is from methanogens, of which 2/3 is by acetate fermentation and 1/3 by CO_2 reduction (7). While the portion generated by methanogen varies, there is strong evidence that it may be the predominant mechanism in some fields. For example, in the Terang-Sirusan Field in the East Java Sea, methane is generated exclusively by methanogens using the CO_2 -reduction pathway (12). Furthermore, recent study of oil and gas fields in the Gulf of Mexico shed light on the rate of methane evolution. It appears that they may be significant recharge of reservoir methane in a timeframe (decades) that is significant to commercial uses (13).

Developments in genetic decoding, gene sequencing, identification of novel enzymes, and selection of desirable traits have the potential to result in enhanced CO_2 to CH_4 conversion processes. The potential exists for both improved biological processes using engineered biological systems, or processes that mimic biologically-based catalysts and processes (biomimetics). For example, advances in the "directed development" of microorganisms offers the potential for enhancing biochemical processes and pathways of interest for commercial applications (14).

In the area of biological or biomimetic advanced concepts, a number of potential CO_2 sequestration pathways have been discussed, including mineralization of CO_2 to carbonates. One such approach is the enzymatic catalysis of CO_2 to carbonic acid and thence to carbonate materials (15). A second major pathway is methanogenesis. Extremophile organisms have been isolated from deep-sea ocean vents where they live at high temperatures and pressures. One such organism, *Methanococcus jannaschii*, was first isolated at a hydrothermal vent in the Pacific Ocean, and is currently the subject of genome mapping under the U.S. DOE Microbial Genome Mapping Program (16). These extremophile characteristics may be compatible with conditions in oil- and gas-producing formations. Alternatively, compatible characteristics could be obtained through directed development.

The conceptual system proposed here would close the carbon-cycle loop for fossil energy by converting CO_2 produced by power plants into CH_4 for subsequent power production. It would consist of the following.

- The development of an enhanced microbial consortium to produce CH_4 at a commercially-useful rate.
- The use of depleting or depleted oil or gas reservoirs, or saline reservoirs, as storage sites for captured CO_2 . CO_2 has historically been widely used in enhanced oil recovery operations.
- The use of the enhanced microbial consortium in a reservoir to convert the stored CO_2 to CH_4 .
- The reservoir would largely be left alone for a period of 10 years to several decades while the microbial consortium operated, with reservoir monitoring to assess gas composition.
- As CH_4 evolved over time, it would be produced through the existing field well and collection structure.

Figure 3 depicts the general concept and the geologic setting. An alternative approach would be to perform the conversion above-ground in rapid-contact reactors. This would assume a biomimetic pathway with kinetics greatly enhanced over the reservoir approach.

CONCLUSIONS

The attainment of "closed-loop" fossil fuel carbon cycles could provide the energy supply needed for economic security and environmental quality over the next century while renewable energy sources develop. Geologic storage of CO_2 with subsequent biological or biomimetic conversion to CH_4 would provide one such closed cycle. While

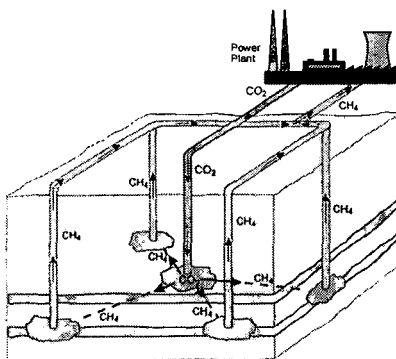


Figure 3. Closed-Loop-Carbon-Cycle Power Production

there appears to be a sound fundamental basis for this and related approaches, several areas of research are indicated.

- A better understanding of emerging sequestration processes in various geological settings is required.
- The kinetics of known microbial conversions appear to be relatively slow; increases of many orders of magnitude will be required for processes of commercial scale.
- Related factors, such as growth cofactors needed to sustain a healthy microbial population, the source of hydrogen for CO₂ conversion, and the mechanisms to remove waste products in a geological setting must be determined.
- While the approach would build on natural geophysical and biochemical processes combined with novel or enhanced enzyme and energy pathways, our present understanding of these processes is fragmented in this context. A systematic assessment of the linkages and relationships of the geologic, chemical, and biological components will be necessary.
- Public acceptance of the process as a safe, benign mechanism for commercial-scale applications must be assured.

If these barriers can be resolved, the concept would provide significant benefits.

- The closed loop process would enable continued use of hydrocarbon fuels without requiring a totally decarbonized fuel product or total conversion of the energy infrastructure to a hydrogen-based economy.
- The approach would expand geologic sequestration options to include essentially unlimited value-added production of a fuel form (beyond what could be achieved through CO₂-enhanced oil recovery or CO₂-enhanced recovery of coal-bed methane, where CO₂ enhances production only of the existing gas- or oil-in-place).
- The process would support sustainable, closed-loop energy production without the large surface-area requirements and impacts of biomass, wind, or photovoltaic systems.
- When combined with other pathways to permanent sequestration (e.g., mineralization), it would provide a more robust basis for a zero-carbon fossil energy infrastructure.

The authors wish to interest researchers from various disciplines in beginning an open and extended dialogue on the potential of novel concepts, such as one discussed here, in developing science and technology options to mitigate global climate change. The role of novel science and technology approaches will be critical to the development of effective mechanisms to stabilize greenhouse gas concentrations.

ACKNOWLEDGMENTS

We are indebted to our associates at the U.S. Department of Energy, with whom we have had discussions and who have provided valuable information on topics related to bacterial genomes and other microbial research: Gregory L. Dilworth, Daniel W. Drell, Anna L. Palmisano, and Nicholas B. Woodward.

We have also received information from numerous researchers outside of the DOE that proved invaluable. We would like to express our appreciation to Dr. Jean K. Whalen, Woods Hole Oceanographic Institute, for information on the topics of marine sediments, marine geomicrobiology and reservoir recharge; to Dr. James G. Ferry of Pennsylvania State University for information on enzyme mechanisms and functional genomics; to Dr. Martin Schoell of Chevron for information on the origins and concentrations of biogenic methane; to Dr. William Gunter of the Alberta Research Council for information on gas generation and characteristics in Canadian formations; to Drs. Keith Kvenvolden and William Dillon of the United States Geological Survey for information on methane occurrence in fluid seeps; to Dr. Roger Sassen of Texas A&M University for information on natural gas hydrates and hydrocarbon seeps in the Gulf of Mexico; to Dr. Gillian M. Bond of New Mexico Tech for information on the catalytic hydration of CO₂ and the formation of carbonates; and to Dr. Frances H. Arnold of the California Institute of Technology for information on protein design and the evolution of new biocatalysts.

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THE SEQUESTRATION OF CARBON DIOXIDE TO THE DEEP OCEAN BY FERTILIZATION

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KEYWORDS: CO₂ sequestration/ Ocean fertilization/ Iron fertilization

ABSTRACT

The sequestration of carbon dioxide (CO₂) to the deep ocean by the fertilization of high nutrient, low chlorophyll (HNLC) ocean waters can be an answer to the concerns arising from the increasing CO₂ content of the atmosphere. This approach has the potential to sequester CO₂ for 1000 to 2000 years for a cost of about \$2.00/ton of CO₂. A technology demonstration is planned to fertilize 5,000 square miles of the equatorial Pacific that is expected to sequester between 600,000 and 2,000,000 tons of CO₂ in a period of 20 days. The concept is that fertilization of HNLC waters with chelated iron will cause a bloom of phytoplankton that sink below the thermocline into deep water. Five recent ocean experiments have observed iron stimulation of phytoplankton growth, but the effects were difficult to quantify in these 9 to 28 square-mile experiments because eddy diffusion along the edges of the patch diluted the bloom. This problem will be minimized in the planned technology demonstration because its large area reduces the impact of exchange at the edges.

INTRODUCTION

The CO₂ content of the atmosphere has increased from about 280 ppm to about 365 ppm during the last 60 years¹. During the 1980's the rate of increase of CO₂ in the atmosphere, in terms of carbon metric tons, was about 3.3 gigatons of carbon per year (GtC/yr). Fossil fuel emissions were about 5.5 GtC/yr (20 Gt CO₂/yr*) and terrestrial emissions were about 1.1 GtC/yr during that period, so about 3.3 GtC/yr, 60% of fossil fuel emissions, were sequestered naturally. Of this, about 2.0 GtC/yr was absorbed by the oceans and 1.3 GtC/yr by the land.² The remaining 40%, 2.2 GtC (8.1 GtCO₂)/yr, contributed to the increasing atmospheric CO₂ concentration. This increase in the CO₂ content of the atmosphere has led to concerns that this increase will result in global climate change, which, over time, can have adverse effects on weather, sea level and human survival. This concern has led to the 1992 Rio Treaty, the IPCC Working Group³ and the Kyoto Protocol of 1997, which call for a reduction of emissions of 34% by 2050 and a reduction of 70% from the then-expected emissions by 2100⁴. These reductions, if put into effect, would have serious adverse effects on the economy of the United States, causing loss of jobs, decrease in our standard of living and a reduction in the life span of our citizens. These required reductions would not address the concerns that demand an approach to permit the reversal of atmospheric CO₂ increase, should this become necessary.

THE CURRENT APPROACH

The current approach to the problem of atmospheric CO₂ increase is to take specific actions now to reduce the risk of adverse consequences in the future. These actions are to increase the efficiency of energy production and use and to change our standard of living to reduce our dependence on energy in our lives. Energy efficiency can often be increased, but we have been doing this for over 200 years, so there is not a lot of gain remaining before we run into thermodynamic barriers. Even at 100% efficiency we still add CO₂ to the atmosphere, so this can never address peoples' concerns. We can also address the other side of the problem, which is to increase the rate at which CO₂ is removed from the atmosphere. If we could increase this enough we could bring the net increase in CO₂ emissions to zero, providing a solution to the problem of peoples' concerns.

CO₂ is removed from the atmosphere by plants using the Sun's energy to convert it to biomass. This biomass may be used as food by bacteria, fungi and animals that obtain energy by reacting it with oxygen from the air and respiring CO₂ back to the atmosphere. Over time, a portion of the biomass formed has been sequestered in the earth and in the ocean bottom, forming fossil fuels that we burn to obtain energy to support our standard of living. Numerous projects have been undertaken to increase tree growth in the tropics, which reduces the CO₂ content of the atmosphere. These projects suffer from a short lifetime, generally 20 to 50 years, and the difficulty of assuring that forest fires, poaching, etc., will not result in an early recycling of the carbon to the atmosphere. Other CO₂ sequestering technologies have been proposed, including injection of liquid CO₂ into geological formations or into the deep ocean. These suffer from high cost, since the flue gases have to be cooled, separated to make pure CO₂, compressed to a liquid, transported to the site and then injected down a well or into the deep ocean. The projected cost is in the range of \$300 per ton of carbon.

* 1GtC = 3.67 Gt CO₂

OCEAN FERTILIZATION

Another approach is to sequester CO_2 to the deep ocean by causing a bloom of plant life that then sinks to the deep waters where it remains for about 1600 years. This process is possible because large areas of the oceans have excess, unused plant nutrients and much less than expected phytoplankton biomass, the so-called HNLC waters. The difference is that the HNLC waters are deficient in one or more of the micronutrients required for plants to grow. While several essential metals may be involved in the limitation of growth in HNLC areas, iron has been shown to be the major micronutrient. Generally, 100,000 moles of carbon biomass require 16,000 moles of fixed nitrogen, 1,000 moles of soluble phosphorous and one mole of available iron. The main difficulty is the iron. Since surface ocean waters are highly oxygenated, any soluble iron is soon converted to Fe^{+++} and precipitates as $\text{Fe}(\text{OH})_3$. A shovel full of earth is about 5.6% iron on the average. The ocean, on the other hand, has 0.000000001 or less moles per liter of iron. The first problem, then, is how to add iron to the ocean so that it will be available to the phytoplankton (plants). The phytoplankton themselves exude organic chelating compounds into the ocean that protect the iron that is there from precipitation. Adding iron in the form of a chelate so that it does not precipitate but remains available for plant fertilization can mimic this natural process.⁵ An essential element that may be in short supply in nutrient-depleted, tropical ocean waters is phosphorous. Most phosphates are soluble and can be added directly to the ocean. Since the phosphate may attack the iron chelate, it may be necessary to keep the concentrations of both fertilizers low. This can be done by adding them to the ocean separately in the form of small floating pellets that release the fertilizing element slowly over a period of days.⁶ This process has been tested in the Gulf of Mexico with good results. The remaining required essential element is fixed nitrogen. Bluegreen algae or, as they are more properly called, cyanobacteria, have the ability to fix nitrogen, so inducing a bloom of nitrogen fixers might supply this requirement.

When the fertilizer mixed with water is added to the tropical ocean surface it mixes rapidly in the warm waters (the mixed layer) and starts the phytoplankton bloom. The plants, mostly diatoms, multiply rapidly, increasing their numbers by two to three times per day, until they run out of one of the required nutrients. They then cease growing, lose the ability to maintain buoyancy and presumably sink through the thermocline. The sinking biomass is trapped in the cold, dense waters where it is eaten by animal life and bacteria. This slowly converts the biomass back to CO_2 in the deep waters. Where high concentrations of biomass reach the bottom and are covered by mud and debris, anoxic digestion may occur. The methane produced is converted to methane hydrates by the high pressure of the deep ocean. It has been estimated that there is more carbon in the methane hydrates of the deep ocean floor than all the terrestrial fossil fuels combined. It is worth noting that the addition of CO_2 in this low concentration, natural process is not expected to have any adverse environmental impact on the ocean, which now has about 85 times as much dissolved inorganic carbon as the atmosphere.

Since our objective is to sequester CO_2 to the deep ocean it is important that we minimize the proportion of the biomass produced that is processed by animal life and bacteria in the mixing layer above the thermocline. This can be done by fertilizing in pulses, so that the slower-growing animal life cannot multiply effectively before the diatoms have bloomed, died and gone below the thermocline, a period of less than 20 days.⁷ We must also test the waters we intend to fertilize in order to add the correct amount and mix to produce the optimum result. To achieve this we select the waters for fertilization to include a strong, shallow thermocline, tropical sunshine and high nutrient, low chlorophyll (HNLC) conditions. These waters can be found in the tropical Pacific near the equator west of the Galapagos Islands. The cool wind-driven currents go directly to the west before reaching the Line Islands of Polynesia. These HNLC waters can sequester about 0.4 $\text{GtCO}_2/\text{yr.}$, a significant proportion of the 8.1 $\text{GtCO}_2/\text{yr.}$ from fossil fuels that is not sequestered naturally.

TECHNOLOGY EXPERIMENTS TO DATE

The technology of ocean fertilization as a means of CO_2 sequestration is still in its infancy. Accurate estimates of the results of ocean fertilization cannot be obtained from bottle experiments. The iron tends to stick to the walls, increasing the response by as much as 100 times. Therefore, ocean voyages were started in 1993 to determine the response. The first voyage in the equatorial Pacific, IronEx I, spread 880 lbs. of Fe as FeSO_4 on a 25 square mile patch resulting in an increase in phytoplankton, but no measurable decrease in the CO_2 content of the water. This was due to the sinking of the patch under an intrusion of barren warmer water. A second voyage in the same area of the equatorial Pacific, IronEx II, spread 990 lbs. of Fe as FeSO_4 on 28 square miles of the ocean surface.⁸ In order to mitigate the effect of iron precipitation, the iron was added in three infusions, half on day zero, one-fourth on day three and one-fourth on day seven. This resulted in a bloom of diatoms. The chlorophyll increased by a factor of 27 times, while the CO_2 partial pressure was reduced by 90 μatm in the patch.

Ocean Farming, Inc. (OFI) has undertaken two voyages in the nutrient-depleted tropical waters of the Gulf of Mexico. Voyage 1 was carried out in the Gulf of Mexico in early January 1998. Three, 9 square mile, patches were fertilized: one with iron, only; one with iron and 6.35 times the molar ratio of phosphorous to iron; and one with iron and 63.5 times the molar ratio of phosphorous to iron. The iron was in the form of a chelate to protect it from precipitation and the phosphorous was in the form of phosphoric acid. The ocean and weather conditions, including a very deep thermocline and high winds, caused the fertilizer to mix much more rapidly, both vertically and horizontally, than planned. The result was a bloom of large diatoms to 4.3 times their initial concentration in a little over one day. After that, the mixing diluted the signal to about 1.5 times the initial chlorophyll concentration. These results, while giving a positive indication of a large bloom were not definitive and did not provide a verifiable measure of phytoplankton increase over the period of the expected bloom of about two weeks.

Voyage 2 was carried out in the Gulf of Mexico in early May 1998. One 9 square mile patch was fertilized using the enhanced chelated iron-containing pellets. The ocean conditions were much more benign (no one got seasick) and we were able to follow the patch for six days. The pellets acted as expected, discharging the chelated iron over a period of four days. The result was a bloom of large diatoms that averaged five times background and reached seven times background. Further increase in phytoplankton was restricted by the absence of the next required fertilizing element, probably phosphorous, nitrate or both. However, extrapolating over the increased size to the patch gave an estimated 600 tons of diatoms per ton of fertilizer pellets, or 1,800 tons of diatoms per ton of chelated iron added to the waters. Both voyages in the Gulf of Mexico were in low nutrient, low chlorophyll (LNLC) waters, which are not favorable to the production of large blooms.

A fifth voyage, SOIREE, has been conducted in the Southern Ocean south of New Zealand. Full reporting is not yet available, but preliminary data indicate that a successful bloom was achieved in those HNLC waters.

These experiments have added greatly to our knowledge of the biodynamics and chemistry of the ocean. Other recent measurements have further increased our understanding. These have included the tethered buoy systems (TAO buoys) as well as the SeaWiFS satellite, instrumented buoys and drifter systems. These systems have, for the first time, provided continuous measurements of the ocean surface as well as at depth, instead of isolated measurements from intermittent ship cruises. This great increase in data has provided enough understanding that we can now design a technology demonstration aimed at proving the CO₂ sequestration potential of ocean fertilization.

PLANNED TECHNOLOGY DEMONSTRATION

All of these previous experimental voyages, while providing a compelling case for iron fertilization in HNLC waters, did not provide a solid basis for evaluating the potential for carbon sequestration. The fertilized patches were all so small that they were all edge; that is, the diffusion in the ocean surface waters is so great that the result of the fertilization, especially the amount of the biomass that sinks below the thermocline, could not be measured. Therefore, we have designed a technology demonstration using the long-lived chelated iron fertilizer in the HNLC waters of the equatorial Pacific Ocean. The fertilized patch will be 5,000 square miles in area and designed to sequester between 600,000 and 2,000,000 tons of CO₂. The patch will be laid by a chemical tanker that will traverse a spiral path⁹ starting at a floating buoy that is maintained as the center of the pattern at all times. When the 5,000 square mile (80 miles in diameter) patch has been completed, in approximately four to five days, the commercial ship will return to port. It will leave a patch with an iron concentration of 2 to 4 nM Fe in the ocean, an increase of about 20 to 40 times background. Based on patch dissipation rates determined from the IronEx studies in the same general Pacific location, the reduction in concentration from diffusion for the center of the patch is expected to be about 2% during the 20 days of the test. A scientific team on a research vessel using the most advanced technology, including direct measurement of the sinking biomass under the patch will measure the response to the fertilization. The research vessel will continuously transact the patch, taking samples to compare with the background measurements made before the patch is laid and, later, outside of the patch. The academic team will measure all relevant environmental impacts until the impacts vanish, which is expected to take about 20 days. The ocean area of the test site is shown in Figure 1. This area is over 2,000 miles from any reef system and in waters 10,000 to 15,000 feet deep that have high oxygen content. Therefore, anoxia that can occur in shallow waters will not be a problem. Red tide and noxious algae typically occur only in shallow waters so should not be a concern. We will not be adding any new organisms to the ocean, only increasing the numbers of those already there. This controlled experiment will parallel the upwellings that occur off of the coast of Peru in all but the El Niño conditions, so we expect the environmental impacts to be benign.

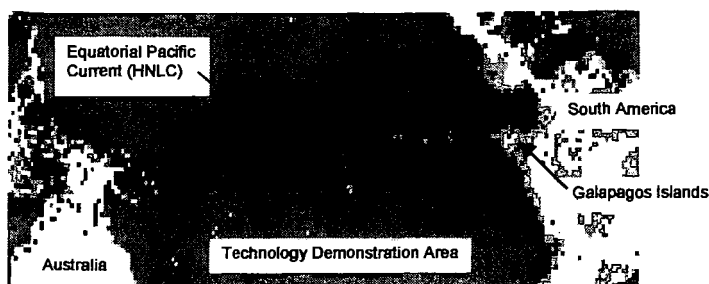


Figure 1. Location of Planned Technology Demonstration

POSSIBLE COMMERCIALIZATION

Should the increasing CO_2 content of the atmosphere be determined to have adverse impacts, the further demonstration of this technology can provide a solution, relieving the concerns regarding the continuous increase of these adverse impacts. CO_2 sequestering could then be carried out in the equatorial Pacific and in other HNLC waters, especially off of Antarctica, the main areas of the oceans that have a high capacity of sequestering CO_2 . For instance, if all the CO_2 in the atmosphere were sequestered in the ocean, it would raise the average concentration of CO_2 in the ocean by only about 1.2%. The ocean chemistry would not be altered significantly and the increase in outgassing of the CO_2 would be minimal.

The cost of sequestering CO_2 on a commercial scale is expected to be about \$1.00 per ton of CO_2 . The sales price for CO_2 sequestering credits, should they become tradable, would be about \$2.00 per ton of CO_2 , to include the cost of verification, overhead and profit. It is expected that these credits would be highly valued since they would not suffer from the problems of fire hazard, leakage and additionality the forest projects for CO_2 sequestering face.

CONCLUSION

Many approaches for dealing with the increase in the CO_2 content of the atmosphere have been proposed, but sequestration by ocean fertilization has received little attention. It is new, far away and poorly understood by many. The initial reaction is that not enough is known to warrant attention at this time. While this reaction may have had merit in the past, the last few years have seen a great increase in knowledge about the oceans, especially the equatorial Pacific, where moored and floating buoy systems, research vessel voyages and continuous satellite monitoring have all greatly increased our knowledge and understanding. The last remaining piece of the puzzle is to quantify the response of this HNLC ocean water to iron fertilization, which can be done by the large experiment described here. We now know enough to design and carry out this technology demonstration experiment, which can lead to solving the problem of peoples' concerns rather than just working on it, thereby saving time and costs while greatly reducing the risk of adverse consequences.

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Thermodynamics of Conversion of Methane Clathrate Hydrate to Carbon Dioxide Hydrate Within Porous Media

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Key Words: carbon dioxide hydrate, equilibrium conditions of gas hydrates decomposition, enthalpies of gas hydrates dissociation.

INTRODUCTION

Environmental concerns about rising concentrations of atmospheric carbon dioxide are stimulating R&D on a variety of carbon dioxide sequestration options. In energy-supply research, it has been estimated that natural gas hydrates in arctic and seafloor formations contain more energy than all other fossil fuel deposits (coal, oil, and natural gas) combined.¹ From data in the literature it is known that the conversion of bulk methane hydrate to bulk carbon dioxide hydrate is thermodynamically favored.¹ Thus, it has been proposed that the sequestration of CO₂ and the production of natural gas might be performed simultaneously by the injection of carbon dioxide into deposits of natural gas hydrates and the conversion of CH₄ hydrate to the hydrate of CO₂.^{2,3}

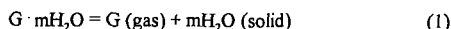
However, natural gas hydrates usually are found distributed within the pores of sediments,¹ and the thermodynamic parameters of methane hydrate are affected by the size of the pores in which the hydrates form.⁴⁻⁶ Recently we have measured the temperature-pressure equilibria and heats of formation of CO₂ hydrates in silica gel of various pore diameters. These measurements show how the temperature-pressure equilibrium of CO₂ hydrate depends on the pore size, and allow us to estimate the effect of pore size on the heat of dissociation of CO₂ hydrate. Bulk natural gas hydrates almost always occur in the "sII" crystal structure, because the presence of as little as one percent propane is sufficient to change the structure from the "sI" form of pure methane hydrate.¹ Measurements on the formation of hydrate(s) in pores by various multi-component natural gases have not yet been performed. Nevertheless, by comparing thermodynamic data for hydrates of CO₂ and CH₄ in porous media, we can explore whether calculations performed for the conversion of bulk natural gas hydrate to bulk carbon dioxide hydrate need to be corrected for pore-size effects.

EXPERIMENTAL METHOD

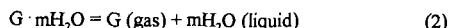
Carbon dioxide hydrate was synthesized within the pores of silica gel following the method described by Handa⁶ for hydrates of methane and propane. The silica gel was obtained from Aldrich; according to the vendor, the pore diameter of the Davisil™ material was 15.0 nm. Pore diameter and surface area also were determined by the BET method.⁷ The mesh size of the silica gel was 200-425, and the purity of the carbon dioxide (Matheson Coleman) was 99.99%. Sample temperatures were established by immersing the pressure cell in the fluid of a NesLab model RTE-140 chiller bath, which kept the temperature constant to within 0.05 K. Bath temperatures were read with a Hart Scientific model 1006 MicroTherm thermometer, traceable to NBS standards, with a sensitivity of 0.001 K. Pressures were measured by means of a calibrated Sert pressure transducer and readout with a sensitivity of 0.0068 MPa and an accuracy of 0.11% of full scale (20.40 MPa).

RESULTS

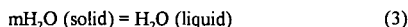
Figure 1 illustrates the equilibrium pressure vs. temperature curves for the hydrates of carbon dioxide (present work) and methane⁶ in 15 nm diameter pores. The carbon dioxide pressure-temperature data were converted to fugacities⁸ and plotted vs. 1000/T (Fig. 2). The carbon dioxide hydrate data in Figs. 1 and 2 are for two different equilibria:



and



where G is the "guest" molecule. Reactions (1) and (2) are in equilibrium at the (lowest) quadruple point. Linear regressions were performed to the data of Fig. 2 above and below the quadruple point, respectively. The regression equations were $\ln f = 17.671 - 4.7237/T$ ($R^2 = 0.9992$) and $\ln f = 18.184 - 4.8599/T$ ($R^2 = 0.9927$), respectively. The quadruple point (i.e., point of intersection of the two regressions) was $T_Q = 266.9$ K, $P_Q = 0.98$ MPa. As suggested by (1) and (2), the quadruple point determined by the equilibrium



is essentially independent of pressure over the change of quadruple point pressure induced either by pore effects or by changes of the "guest" component (CO_2 or CH_4). Hence, the quadruple point temperature is principally determined by the effect of pore size on the melting point. Using differential scanning calorimetry, Handa measured the melting point of ice in 15 nm diameter pores to be 267.5 K.⁹ Thus, the value for the quadruple point temperature found from the carbon dioxide hydrate data compares favorably with the expected value. From Handa's pressure-temperature data for methane hydrate we calculate $T_Q = 267.4$ K. The quadruple point temperature is $T_Q = 273.1$ K for bulk hydrates of CO_2 and CH_4 . Thus, the effect of pore size on the quadruple point temperature is simple: it is essentially the same for all guest-molecule compositions. For 15 nm diameter pores, the quadruple point temperature is lowered by 5.6 K.

Next, the enthalpies for equilibria (1) and (2) were estimated from the data plotted in Fig. 2, by means of the Clausius-Clapeyron equation. As listed in Table 1, these calculations yielded the values 35.59 kJ/mole for equilibrium (1) and, 39.10 kJ/mole for equilibrium (2) of CO_2 hydrate. Also listed in Table 1 are the enthalpies that we have calculated from Kamath's data for methane and carbon dioxide hydrates in sand packs¹⁰ and calorimetric data by Handa⁵ for methane hydrate in 15 nm silica gel. Additional data for CO_2 hydrates in porous media may be found in ref. 11.

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Table 1. Heats of Dissociation (kJ/mole) for Hydrates of Methane and Carbon Dioxide in Sand and in 15 nm Diameter Pores

Guest	Medium	Heat of Dissociation (kJ/mole)	
		reaction (1)	reaction (2)
CH_4	15 nm pores ^(a)	15.83	45.92
CH_4	sand ^(b)	15.22	68.84
CO_2	15 nm pores ^(c)	35.59	39.10
CO_2	sand ^(b)	25.43	82.43

^(a)Heat measured calorimetrically by Handa⁵

^(b)Heats calculated in the present work from the equilibrium pressure-temperature data of Kamath¹⁰

^(c)Heat obtained in the present work

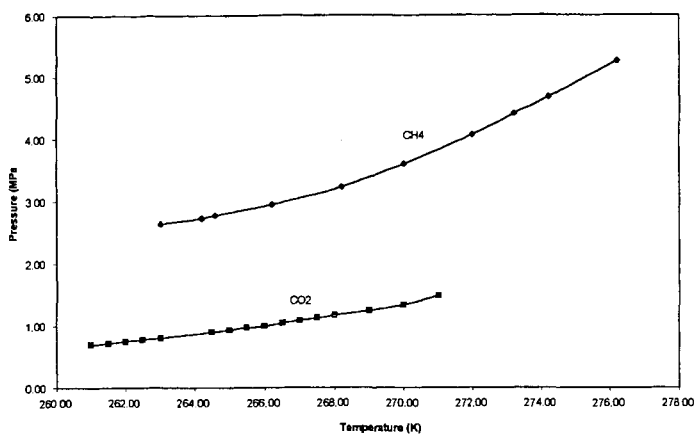


Figure 1. Equilibrium pressure-temperature for hydrates of CO₂ and CH₄ in 15 nm diameter pores of silica gel.

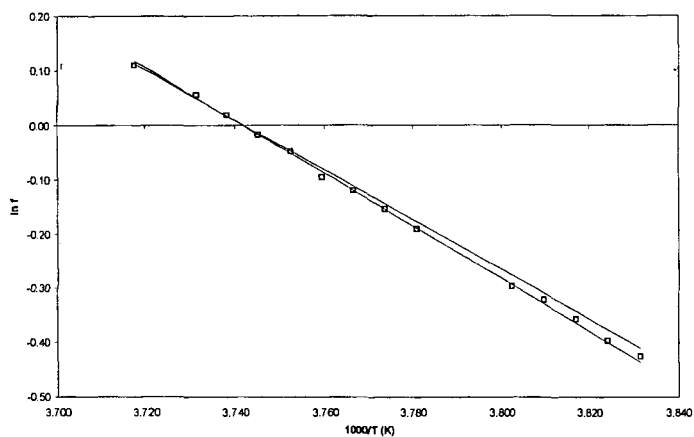


Figure 2. Logarithm of the fugacity, f , vs. inverse temperature, $1/T$, for CO₂ hydrate in 15 nm diameter pores of silica gel.

Reformation and Replacement of CO₂ and CH₄ Gas Hydrates

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Keywords: Gas Hydrate, Methane Hydrate, Carbon Dioxide Hydrate, Reformation, Replacement

INTRODUCTION

Large amounts of gas hydrates, clathrate compounds of water and gases formed under high pressure and low temperature, are found in marine sediments and permafrost. To extract methane gas from its reservoir in a practical method, it is necessary to obtain fundamental information on the mechanism underlying the formation and dissociation of gas hydrates and their properties, including kinetics and crystal growth. We have proposed an advanced method of gas hydrate production, by which methane gas is extracted from the reservoir by replacing methane with carbon dioxide at the molecular level. This method would be feasible to achieve the sequestration of carbon dioxide into the sediments. The main purposes of this research are to elucidate the mechanism underlying hydrate reformation and replacement and accumulate practical data for completing the original concept of the proposed method. We have carried out experiments on the dynamics on reformation and replacement of gas hydrates using an apparatus consisting of a high pressure vessel and a Raman spectroscopy. In this paper we present the experimental results concerning the behavior of gas hydrate reformation and replacement, and some discussion on the dynamics and the mechanism of gas hydrate formation.

EXPERIMENTAL

The experimental apparatus, in which the formation and replacement of gas hydrate could be observed, was designed and constructed, so that the several conditions of pressure, temperature and concentration of gases could be precisely controlled. Fig.1 illustrates the schematic diagram of the apparatus and measuring system used in the experiment. The pressure cell, made of stainless steel with a 3.2 ml internal volume, can be used at a pressure condition of up to 20 MPa. It contains a glass window for observing Raman scattering of monochromatic lights, a thermoelectric temperature control module, and some nozzles for the introduction of gas and liquid components. The pressure cell is installed on a constant temperature plate filled with a cooling agent methanol, where the temperature can be controlled with an accuracy of ± 0.1 K. It is equipped with transducers for detecting and controlling pressures with an accuracy of ± 0.05 MPa. The observation system of the Raman spectroscopy and a CCD camera are mounted in the apparatus as shown in Fig.2.

As a preliminary experiment, samples of CH₄ gas hydrate were synthesized from fine ice crystals and pressurized CH₄ gas, and stored as solid-phase pellets under extremely low temperature. The procedures of the experiment on reformation and replacement of gas hydrates are as follows. A pellet of CH₄ gas hydrate sample with a volume of 0.8 ml is placed into the pressure cell at a low temperature (< 253 K), and remaining volume of the pressure cell is filled with pressurized CO₂ gas. The internal pressure and flow rate of the gas can be adjusted using a fluid supplier system. The flow rate of CO₂ is set to approximately 5 ml/min. The reformation of CO₂ gas hydrate is observed during the changes in temperature of entire system. CH₄ gas hydrate no longer exists in this condition. The experiment on replacement is conducted under the conditions where both CO₂ and CH₄ gas hydrates can exist in the solid phase. An optical cell and the Raman spectroscopy system are installed on the glass window for detecting the nucleation and change of component of the hydrate structure. The gas components are analyzed by gas chromatography.

RESULTS AND DISCUSSION

a) Reformation of CO₂ and CH₄ gas hydrates

There are many differences of formation properties between CO₂ and CH₄ gas hydrates, such as the phase equilibrium and the formation rate. Fig.3 shows the pressure-temperature relationship of formation obtained at the first run of CO₂ and CH₄ gas hydrates. A first run is a situation of nonequilibrium formation without any gas hydrate nuclei in dissolved solution. The upper curve represents the relationship between nonequilibrium formation temperature T_f and pressure P_f , the lower curve, that between dissociation temperature T_d and pressure P_d . The center curve corresponds to the three-phase equilibrium estimated using the thermodynamic theoretical approach (Sloan). It can be seen that the relation between $P_f(P_d)$ and $T_f(T_d)$ is approximately linear in a semilog plot. In addition, it was found that the formation relation greatly differs from the theoretical data of phase equilibrium. The differential temperatures between nonequilibrium

formation and dissociation for CO_2 gas hydrate were slightly higher than those for CH_4 gas hydrate. At the second and third runs, reformation of gas hydrates occurred under conditions of higher temperatures and/or lower pressures than those at the first run. However, a supercooling temperature higher than 1.5 K was necessary for gas hydrate reformation in the case of CO_2 . These properties may reveal interesting phenomena concerning the mechanism of gas hydrate nucleation under nonequilibrium conditions.

b) Solid-phase formation of CH_4 gas hydrate samples

CH_4 gas hydrate samples were synthesized in the solid phase for the replacement experiment using fine grains of ice crystal (average diameter: 0.1 mm) and the solution in which CH_4 gas hydrates were dissociated at a temperature slightly higher than the equilibrium temperature. It took a relatively short time to achieve nucleation of gas hydrate using the dissociated solution. When the temperature was set 2.0 K lower than the equilibrium temperature, the reformation of CH_4 gas hydrate could be achieved within 24 hours. Fig.4 shows the result of Raman spectroscopic analysis for CH_4 gas hydrate obtained using the procedure. A sharp Raman shift appears around $2905/2915\text{ cm}^{-1}$, indicating the existence of Type-I CH_4 gas hydrates. According to a more precise analysis, the hydration number of the obtained samples was in the range of 6.4 to 6.0, that is, the ratio of occupancy in small cages can be estimated to be approximately 85-95 percent.

c) Formation rate of CO_2 gas hydrate in quasi-liquid phase

The formation rate of CO_2 gas hydrate was measured in situ observation using Raman spectroscopy; results are shown in Fig.1. The nucleation of gas hydrate was initiated from fine ice crystals under a temperature lower than 273 K. After setting ice crystals into the pressure cell, CO_2 gas was introduced to maintain the pressure inside the cell at 1.6 MPa. Fig.5 illustrates the trend of the Raman shifts obtained from 10 minutes to 2170 minutes after nucleation. Four Raman shift peaks were observed, in which peaks of around 1276 cm^{-1} and 1381 cm^{-1} are due to the existence of guest in the CO_2 gas hydrate structure. It was found in Fig.5 that the values of peak strength increase with time after the nucleation of gas hydrate. As the peak strength closely corresponds to the numbers of molecules in the structure, the formation rate of gas hydrate can be estimated from the peak strength. Fig.6 shows the formation rates of CO_2 gas hydrate obtained at temperatures from 254.5K to 274.5K. The formation rates of gas hydrate changed greatly with temperature, especially in the range between 269 K and 275 K. This suggests that the existence of quasi-liquid phase water, a type of slightly melting ice, plays an important role in promoting formation of gas hydrate at the gas-solid interface. Based on the behavior of CO_2 formation, the optional temperature for the replacement process was set around 273-275 K.

d) Replacement of CO_2 and CH_4 gas hydrates in solid phase

The replacement experiment on CO_2 and CH_4 gas hydrates was carried out using a bulk scale testing apparatus. Samples of CH_4 gas hydrate were synthesized in the solid phase from fine ice crystals and the dissociated solution. A preliminary process was performed under the conditions mentioned in the experimental procedure. During the process of replacement, the pressure of CO_2 was 2.0 MPa and the temperature was $274 \pm 0.5\text{ K}$. Fig.7 illustrates the Raman shifts obtained from the replaced hydrate sample observed 1 hour following CO_2 introduction. Two typical peaks appeared in the Raman spectra, $2905/2915\text{ cm}^{-1}$ for CH_4 hydrate and around $1275/1380\text{ cm}^{-1}$ for CO_2 hydrate. This means that both CH_4 and CO_2 gas hydrates coexist in the structure of the replaced hydrate sample. Based on quantitative analysis, the ratio of occupancy for $\text{CO}_2 / \text{CH}_4$ gas hydrates in the replaced hydrate sample were 40 and 45 percent, respectively. The portion of CO_2 gas hydrate in the sample increased with time. Fig.8 shows the trend of $\text{CO}_2 / \text{CH}_4$ components in the solid hydrate after CO_2 introduction as a function of time. The data were obtained from in situ observation and the analysis of peak strength of Raman shifts. This result indicates that the replacement of guest elements in solid gas hydrates could be achieved within a short period of 12 hours, if the pressure and temperature are precisely controlled in the pressure cell. It is also considered that a period of 2 hours is sufficient for nucleation of CO_2 hydrate at the surface of sample, and then crystal growth proceeds as a result of CO_2 transport into the solid hydrate. Because the transport of CO_2 gas should be fast in porous media, the in situ replacement of CO_2 gas hydrate may be used for the extraction of gas hydrates from their reservoirs. More systematic researches are necessary to elucidate the phenomenon underlying gas hydrate replacement.

CONCLUSIONS

Experimental studies on the dynamics and behavior of reformation and replacement of gas hydrates was carried out using a specially designed apparatus. It was shown that reformation of gas hydrates easily occurred in the quasi-solid structure when the dissociated solution is used. The rate of reformation of CO_2 gas hydrate was observed by Raman spectroscopy. The results of the bulk scale experiment showed that replacement of CO_2 gas hydrate could be achieved within a period of 12 hours in pure samples of CH_4 gas hydrate that had been synthesized as solid crystal, if

the pressure and temperature are precisely controlled in the pressure cell. The replacement of guest elements in CO_2 and CH_4 gas hydrates may be quite innovative from both aspects, the extraction of gas hydrates and sequestration of CO_2 , to maintain the global environment and stability of marine sediments.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. F. Kiyono and Mr. H. Haneda in NIRE for assistance in developing the original concept of the extraction system, and Dr. K. Nagashima and Dr. Seong-Pil Kang for advice in completing the theoretical analysis.

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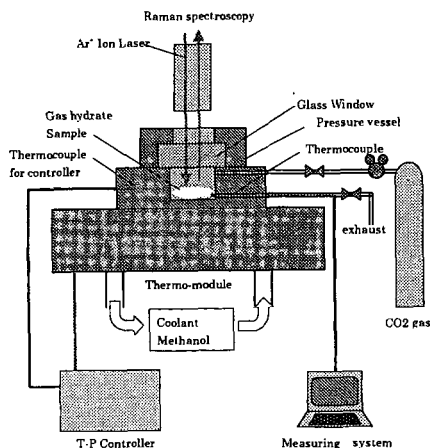


Fig.1 Schematic diagram of the experimental setup for gas hydrate formation.

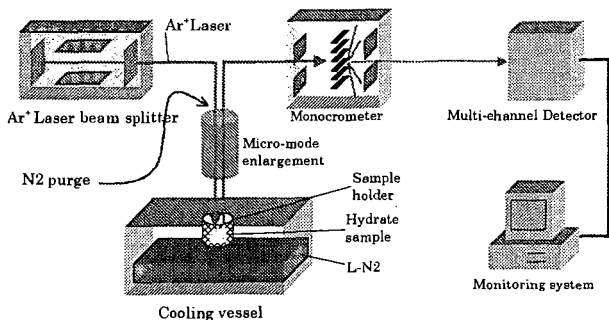


Fig.2 Raman spectroscopy apparatus for observing gas hydrate structure and component.

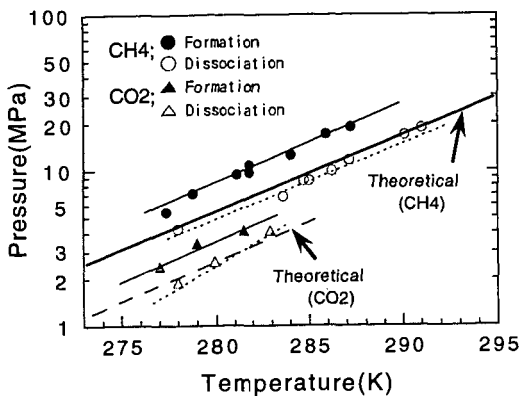


Fig.3 The relations of formation/dissociation P and T for CO_2 and CH_4 gas hydrates.

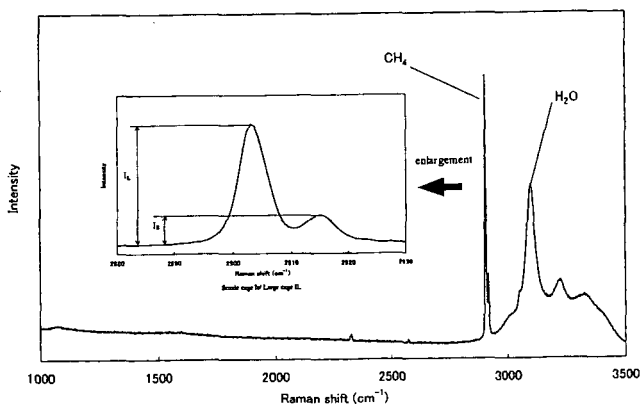


Fig.4 Raman shift for a sample of CH_4 gas hydrate made from ice crystals

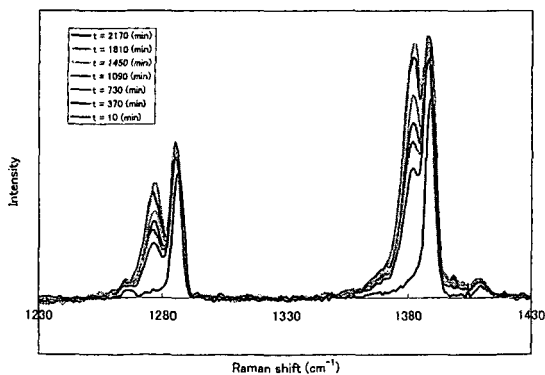


Fig.5 Changes in Raman shifts observed for CO_2 gas hydrate formation.

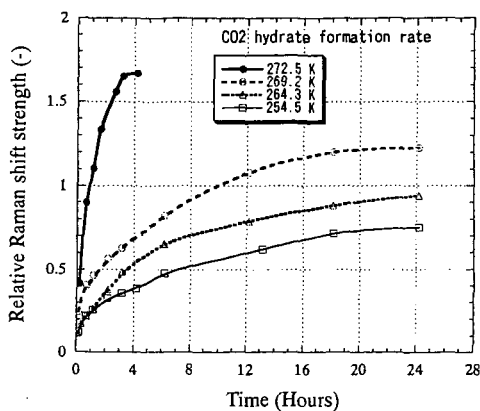


Fig.6 The trend curves of the formation rate of CO₂ gas hydrate under different temperatures.

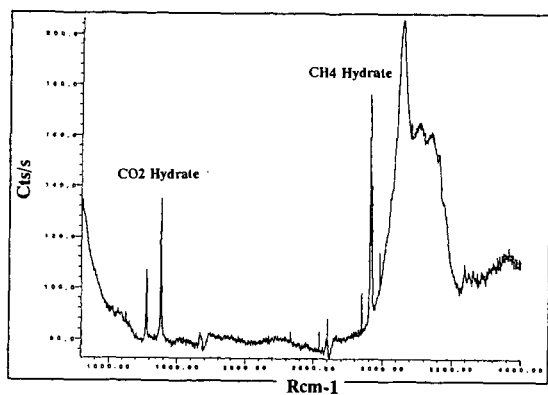


Fig.7 Raman shift for a sample of replacement from CH₄ to CO₂ gas hydrates.

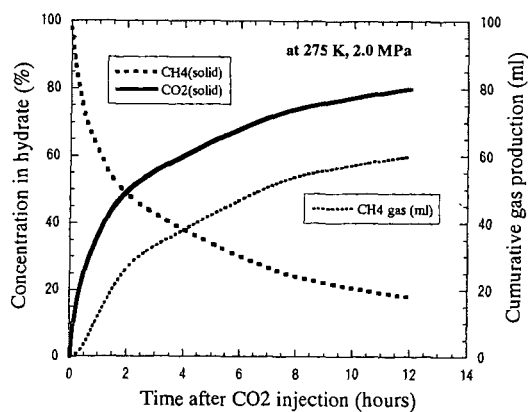


Fig.8 The trend curves of CO₂ and CH₄ components in replaced gas hydrate sample and the cumulative CH₄ production.